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JOURNAL OF INORGANIC AND NUCLEAR CHEMISTRY

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THE RATIO OF INDUCED FISSION VS. SPONTANEOUS FISSION IN PITCHBLENDE AND NATURAL OCCURRENCE OF RADIOCHLORINE*

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(*Received* 4 *March* 1960)

Abstract—Chlorine was isolated from kilogram quantities of both Canadian and African pitchblende, exhaustively purified, and counted. The specific activity of chlorine obtained from African pitchblende was found to be (7 ± 1) disintegrations per minute per gramme of chlorine, while that from Canadian pitchblende was (4 ± 1) disintegrations per minute per gramme of chlorine. The ratio of induced fission of ^{235}U vs spontaneous fission of ^{238}U in these minerals was calculated from the radiochlorine data. A value of 0·33 was obtained for the African pitchblende and a value of 0·19 for the Canadian pitchblende.

IT has been established by DAVIS and SCHAEFFER[1] that cosmic ray neutrons induce measurable ^{36}Cl activity (half-life 308,000 years) in certain surface rocks. KURODA *et al.*[2] have reported the occurrence of ^{36}Cl in Great Bear Lake pitchblende, in which the major neutron sources are the spontaneous fission of ^{238}U and (α, n) reactions. Studies on the radiochlorine in uranium minerals are of a special interest, since the ratio of induced fission of ^{235}U vs. spontaneous fission of ^{238}U in the minerals may be estimated from the radiochlorine data.

The primary purpose of the present study is to see if the above ratio calculated from the radiochlorine data agrees with the results from mass-spectrometric data, which have been reported by FLEMING and THODE[3], and by WETHERILL[4].

EXPERIMENTAL

Chlorine was isolated from kilogramme quantities of pitchblende, carefully purified, and counted in the following manner:

Purification and counting as silver chloride

Pitchblende was dissolved in dilute nitric acid with a reflux system, keeping the reaction flask in an ice-bath. The insoluble residue was removed by filtration and the filtrate was treated with sulphuric acid to precipitate the lead sulphate. The solution was filtered and silver chloride was precipitated by the addition of silver nitrate to the filtrate. The nitric acid insoluble fraction of the pitchblende was treated with dilute ammonium hydroxide solution and filtered. The filtrate was acidified with nitric acid and chlorine was precipitated as silver chloride. The two silver chloride precipitates were combined, dissolved in ammonium hydroxide and the solution filtered, heated and silver chloride reprecipitated by the addition of nitric acid. After digestion of the precipitate, the silver chloride was

* This paper represents a part of the dissertation to be submitted by B. T. KENNA to the Graduate School of the University of Arkansas in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

[1] R. DAVIS, JR. and O. A. SCHAEFFER, *Ann. New York Acad. Sci.* **62**, 105 (1955); BNL-340, T-59, June (1955).
[2] P. K. KURODA, R. R. EDWARDS, B. L. ROBINSON, J. H. JONTE and C. GOOLSBY, *Geochim. Cosmochim. Acta* **11**, 194 (1957).
[3] W. H. FLEMING and H. G. THODE, *Phys. Rev.* **92**, 378 (1953).
[4] G. W. WETHERILL, *Phys. Rev.* **92**, 907 (1953).

filtered, dried, weighed, mounted on filter paper (Whatman No. 1, 4·25 cm), placed in a 2 in. stainless steel planchet, and counted for 24 hr. The silver chloride precipitate was then redissolved in ammonia, and the purification cycle was repeated.

Purification and counting as ammonium chloride

The silver chloride precipitate, after being counted, was dissolved in ammonia, a calculated amount of clean magnesium turnings added, and the solution was allowed to stand overnight in an empty vacuum dessicator (to keep carbon dioxide absorption to a minimum). The solution was filtered and evaporated to a volume of about 50 ml, and a calculated volume of concentrated sulphuric acid was added. The chlorine was then distilled off as the HCl–water azeotrope. After the distillation was complete, anhydrous ammonia gas (Matheson) was passed through the distillate and the solution

TABLE 1.—CONTROL EXPERIMENTS

Sample	Counting form	Weight (mg)	Net (counts/min)
(1) Commercial NaCl 204 mg plus NH_4Cl, 250 mg	AgCl	1287	0·02 ± 0·06
(2) Thermal water, Lacco Ameno, Italy*	AgCl Cycle No. 1	201	0·33 ± 0·07
	AgCl Cycle No. 2		0·01 ± 0·06
	AgCl Cycle No. 3		−0·01 ± 0·06

* Contained 1·4 μc/l. of radon, when the sample was collected.

evaporated to near dryness in a quartz evaporating dish. The ammonium chloride was mounted in the same manner as was the silver chloride, dried and weighed. The percentage recovery of chlorine was usually 91–93 per cent. The ammonium chloride, after being counted, was dissolved in distilled water and the distillation procedure repeated.

Counting equipment

Tracerlab Low Background β-Counting Equipment (CE-14) was used for the radioactivity measurements. It had a background of two counts per minute in anti-coincidence with surrounding cosmic ray counters.

The counter was calibrated by a method similar to that described by HEYDEGGER and KURODA[5].

A standard solution of sodium chloride (1 ml = 100 mg AgCl) was prepared, and various aliquots were taken. To each aliquot was added 1 ml of a standard ^{36}Cl solution (344 dpm ^{36}Cl/ml determined by 4π counting), and silver chloride precipitated by adding 0·1 M silver nitrate solution. The silver chloride was filtered, washed, dried, weighed, and counted.

A standard solution of ammonium chloride (1 ml = 50 mg NH_4Cl) was prepared, and various aliquots were taken. To each aliquot was added 1 ml of the standard ^{36}Cl solution. Anhydrous ammonia gas was passed through each solution for 10 sec and the solutions were evaporated until crystals of ammonium chloride formed on the surface of the solution. On cooling, the slurry was poured and scraped with a rubber policeman onto filter papers in a 2 in. planchet. The samples were dried in an oven at 120°C, weighed and counted.

Control experiment

Chlorine samples from reagent grade commercial salts, and thermal water from Lacco Ameno, Ischia, Italy, were examined for the presence of radioactivity. No activity was found in the chlorine fraction, as shown in Table 1.

EXPERIMENTAL RESULTS AND DISCUSSION

Experimental results obtained are summarized in Table 2.

Although the activity of the chlorine samples isolated from pitchblende was

[5] H. R. HEYDEGGER and P. K. KURODA, *J. Inorg. Nucl. Chem.* **12**, 12 (1959).

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extremely small, it followed chlorine chemistry, and the weak activity of the silver chloride persisted after the purification cycle was repeated twelve times. The specific activity of the chlorine remained constant after the silver chloride sample was purified further by employing the ammonium chloride purification procedure twice. The specific activity of the chlorine sample showed no sign of decay, as shown in Table 2.

TABLE 2.—CHLORINE-36 IN PITCHBLENDE

Sample	Purification cycle No.	Counting form	Weight (mg)	Chemical yield(%)	Net counts/min	Days since isolation from mineral	Specific activity dpm/g chlorine
(1) Belgian Congo, pitchblende, 2000 g	1	AgCl	2739	—	22·9 ± 1·6	0	1220
	2	AgCl	2459	90·0	5·2 ± 0·7	1	275
	5	AgCl	1772	64·8	0·12 ± 0·06	7	6·4
	10	AgCl	1657	60·5	0·17 ± 0·06	18	9·0
	11	AgCl	1632	59·8	0·11 ± 0·06	19	5·8
	12	AgCl	1615	59·0	0·15 ± 0·06	22	7·9
	14	NH_4Cl	109·9	10·8	0·11 ± 0·06	100	6·7
					0·12 ± 0·05	101	7·3
					0·12 ± 0·05	102	7·3
					0·11 ± 0·05	103	6·7
					0·11 ± 0·04	104	6·7
					0·11 ± 0·04	105	6·7
					0·10 ± 0·06	111	6·1
					0·13 ± 0·06	113	7·9
					0·09 ± 0·06	115	5·5
					0·13 ± 0·06	130	7·9
					0·11 ± 0·06	132	6·7
					0·10 ± 0·06	134	6·1
					0·14 ± 0·06	136	8·5
					0·11 ± 0·06	141	6·7
(2) Great Bear Lake pitchblende, 4540 g		NH_4Cl	577	43·4	0·75 ± 0·12 (*)	—	4·1 ± 0·7
		NH_4Cl	232	17·4	0·30 ± 0·10 (*)	—	4·0 ± 1·3

* Counted with a Libby screen wall counter. KURODA *et al.*[2]

The average specific activity of chlorine in Belgian Congo pitchblende, calculated from the silver chloride and ammonium chloride counting data shown in Table 2, and from the chlorine content of the mineral (0·03 %), is (7 ± 1) disintegrations min^{-1} g^{-1} of chlorine, whereas that of chlorine in Great Bear Lake pitchblende is (4 ± 1) disintegrations min^{-1} g^{-1} of chlorine.[2]

SCHAEFFER and co-workers[6] have recently reported that two rains collected in the summer of 1957 contained 2·0 and 8·0 disintegrations min^{-1} of ^{36}Cl per gramme of total chlorine. These levels of activity are several orders of magnitude larger than expected from cosmic-ray production and are probably produced by neutron

[6] O. A. SCHAEFFER, O. S. THOMPSON and N. LARK, Paper presented at the Annual Meeting of the Geochemical Society, Pittsburgh, Pennsylvania (1959).

irradiation of sea spray in oceanic nuclear explosions. The specific activity of chlorine in pitchblende is thus approximately the same as that in rain. However, the possibility that the ^{36}Cl in pitchblende came from rain appears to be remote.

If one assumes that the ^{36}Cl found in Belgian Congo pitchblende, i.e. 7 ± 1 disintegrations min^{-1} g^{-1} chlorine, or 2·1 disintegrations min^{-1} of ^{36}Cl per kilogramme of pitchblende, has originated from rain water containing 8·0 disintegrations min^{-1} of chlorine per gramme of total chlorine, then approximately 250 mg of chlorine from recent rain water must have been absorbed by each kilogramme of pitchblende. According to SUGAWARA[7], the average chlorine content of rain water is 0·76 mg $l.^{-1}$ Thus, 250 mg of chlorine corresponds to a volume of approximately 330 l. for every kilogram of pitchblende. According to the recent studies on fission products in rain water by KURODA[8], the ^{90}Sr content of rain water was of the order of magnitude of 14·7 disintegrations min^{-1} $l.^{-1}$ in 1958. Thus, the ^{90}Sr content of the pitchblende has to be 4·85 disintegrations min^{-1} g^{-1} of pitchblende. KURODA and EDWARDS[9] found however, approximately 7×10^{-3} disintegrations min^{-1} of ^{90}Sr per gramme of Great Bear Lake pitchblende, and the authors[10] have recently found less than 10^{-2} disintegrations min^{-1} of ^{90}Sr per gramme of Belgian Congo pitchblende. For the above stated reasons, we have concluded that the ^{36}Cl did not come from rainfall, but was produced within the pitchblende.

Assuming that thermal capture is the ultimate fate of each neutron produced, the ratio (R) of the number of induced fission (I) vs. the number of spontaneous fission (S) in a mineral may be calculated from the following relationships:

$$I = A \frac{^{235}N(\sigma_f)_{235}}{^{35}N(\sigma_a)_{35}} \times \frac{X}{100} \tag{1}$$

$$S = 138\ ^{235}N \frac{\ln 2}{T} \tag{2}$$

$$R = \frac{I}{S} = \frac{ATX(\sigma_f)_{235}}{13800 \ln 2\ ^{35}N(\sigma_a)_{35}} \tag{3}$$

where: ^{35}N and ^{235}N are the number of atoms of ^{35}Cl and ^{235}U per gramme of mineral, respectively, $(\sigma_a)_{35}$ is the thermal neutron absorption cross-section of ^{35}Cl, $(\sigma_f)_{235}$ is the thermal fission cross-section of ^{235}U, A is the specific activity of chlorine (disintegrations per minute per gramme of chlorine), X is the chlorine content of mineral (in per cent), and T is the spontaneous fission half-life of ^{238}U (in minutes).

Equation 3 can be further simplified by introducing the known values of $(\sigma_f)_{235} = 590$ barns, and $(\sigma_a)_{35} = 44$ barns. Thus,

$$R = \frac{I}{S} = 0{\cdot}140 \frac{AT}{N^{35}} \times \frac{X}{100} \tag{4}$$

The value of T has been measured by a number of investigators. SEGRE[11] reported a value of $(8{\cdot}04 \pm 0{\cdot}3) \times 10^{15}$ years, and PERFILOV[12] reported a value of $(1{\cdot}3 \pm 0{\cdot}2) \times 10^{16}$ years.

[7] K. SUGAWARA, *Kagaku (Science)* **18**, 485 (1948).
[8] P. K. KURODA, ANL-5920, October (1958).
[9] P. K. KURODA and R. R. EDWARDS, *J. Chem. Phys.* **22**, 1940 (1954).
[10] B. T. KENNA and P. K. KURODA. Unpublished data (1960).
[11] E. SEGRE, *Phys. Rev.* **86**, 21 (1952).
[12] N. A. PERFILOV, *J. Exp. Theor. Phys.* **17**, 746 (1947); *Chem. Abstr.* **42**, 2864 (1948).

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KURODA and co-workers[5,9,13,14] have recently reported the equilibrium ratios of a number of short-lived fission products to ^{238}U in natural and in depleted uranium salts (99·989 per cent ^{238}U).

The results obtained by KURODA and co-workers are shown in Table 3 and in Fig. 1.

The results are sufficient to show the general shape of the mass-yield curve for

TABLE 3.—EQUILIBRIUM RATIOS OF THE FISSION PRODUCTS/^{238}U IN NON-IRRADIATED NATURAL AND DEPLETED URANIUM

Mass no.	Nuclide measured	Equilibrium ratio (10^{-4} disintegrations $sec^{-1}g^{-1}$) ^{238}U
89	Sr	4·1 ± 1·0*
90	Sr	4·8 ± 0·4*
91	Sr	4 ± 3
92	Sr	8 ± 3
99	Mo	4·4 ± 0·4
131	I	0·3 ± 0·1
132	I	2·5 ± 0·3
133	I	1·0 ± 0·2
134	I	3·6 ± 0·4
135	I	3·5 ± 0·4
140	Ba	6·2 ± 0·7

* Great Bear Lake pitchblende was used for the experiments and the contribution of induced fission introduces some uncertainty. If one accepts the results shown in Table 4, these values in depleted uranium should be approximately 20 per cent smaller. The strontium isotopes are now being isolated from Belgian Congo pitchblende, and the ratios $^{89}Sr/^{238}U$ and $^{90}Sr/^{238}U$ in this mineral will be measured.

spontaneous fission of ^{238}U and to make a preliminary estimate of the spontaneous fission half-life by the use of the following relationship:[15]

$$^{238}N\frac{\ln 2}{T} = \sum_{i=130}^{150} N_i\lambda_i \tag{5}$$

where, ^{238}N is the number of atoms of ^{238}U, and $N_i\lambda_i$ is the cumulative activity of the fission products at mass number i in equilibrium with ^{238}U.

An estimate of the value of $\sum_{i=130}^{150} N_i\lambda_i$ can be made assuming that the value of $N_i\lambda_i$ at each mass number will be represented by the smooth broken line in Fig. 1. A value of 72×10^{-4} disintegrations $min^{-1}\ g^{-1}$ of ^{238}U was thus obtained. Introducing this value into equation (5), one obtains a value of $T = 8 \times 10^{15}$ years for the spontaneous fission half-life of ^{238}U, which is in excellent agreement with the value reported by SEGRE[11].

Introducing the value of $T = 4{\cdot}2 \times 10^{21}$ min into equation (4) we have,

$$R = \frac{I}{S} = 5{\cdot}88 \times 10^{18} \times \frac{AX}{^{35}N} \tag{6}$$

[13] F. T. ASHIZAWA and P. K. KURODA, *J. Inorg. Nucl. Chem.* **5**, 12 (1957).
[14] P. L. PARKER and P. K. KURODA, *J. Inorg. Nucl. Chem.* **5**, 153 (1958).
[15] P. K. KURODA, Annual Progress Report, AEC Contract (AT-40)-1313, February (1959).

The values of R in Belgian Congo pitchblende and in Great Bear Lake pitchblende, calculated from equation (6), are shown in Table 4.

The values of R thus obtained are in excellent agreement with values obtained by previous investigators by entirely different methods.

WETHERILL[4], using the mass-spectrometric measurements of xenon isotopes in

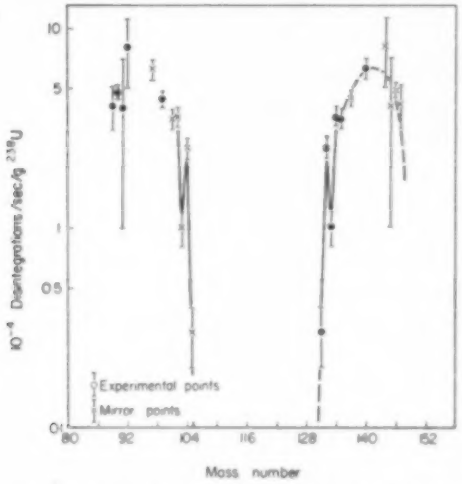

FIG. 1.—Equilibrium ratios of the fission products/^{238}U in non-irradiated natural and depleted uranium salts. (A value of two for the number of spontaneous fission neutrons emitted has been used in order to plot the mirror points.)

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TABLE 4.—THE RATIO (R) OF INDUCED FISSION VS. SPONTANEOUS FISSION IN PITCHBLENDE

Sample	A Disintegrations min^{-1} g^{-1} of chlorine	X (%)	^{35}N Number of atoms of ^{35}Cl per gramme of mineral	R
(1) Belgian Congo pitchblende	7 ± 1	0·03	$3{\cdot}8 \times 10^{18}$	0·33
(2) Great Bear Lake pitchblende	4 ± 1	0·02	$2{\cdot}5 \times 10^{18}$	0·19

uranium minerals, reported that approximately 35 per cent of the fission in Belgian Congo pitchblende (44% U) was neutron-induced. Thus,

$$R = \frac{I}{S} = \frac{I}{S+I}\left(1 - \frac{I}{S+I}\right)^{-1} = 0{\cdot}35/(1 - 0{\cdot}35) = 0{\cdot}54.$$

The fact that the value of R for Belgian Congo pitchblende obtained by WETHERILL ($R = 0{\cdot}54$) is somewhat higher than the value obtained in Table 4 ($R = 0{\cdot}33$) may well be due to the fact that the method employed by WETHERILL yields an average value of R throughout the entire geological life-span of the mineral, which is believed to be approximately 600 million years according to the lead uranium age of the mineral,

whereas the radiochlorine data yields an average value of R during the recent time-interval comparable to the half-life of ^{36}Cl (308,000 years). Due to the relatively short half-life of ^{235}U as compared with ^{238}U, the $^{235}U/^{238}U$ ratio in uranium minerals would have been greater than the ratio in today's minerals by a factor of approximately two.

FLEMING and THODE[3] reported that the ratio of induced fission to spontaneous fission in Great Bear Lake pitchblende (a mill concentrate; original uranium content unknown) was approximately 10 per cent. The value of $R = 19$ per cent obtained by the radiochlorine method is higher than the value obtained by FLEMING and THODE, and is probably due to the difference in uranium contents of samples used.

PURKAYASTHA and MARTIN[16] reported the results of their studies on the natural production of ^{129}I in pitchblende. These workers used the activation analysis method for the determination of ^{129}I, and compared their results with those for ^{129}Xe determined mass-spectrometrically by FLEMING. The mass-spectrometric method yielded a value of $R = 0{\cdot}32$ for pitchblende A (82 % U) and a value of $R = 0{\cdot}49$ for pitchblende B (64 % U), whereas the ^{129}I method yielded a value of $R = 0{\cdot}53$ for pitchblende A and $R = 0{\cdot}59$ for pitchblende B. Considering the fact that the uranium contents of the pitchblende samples used by PURKAYASTHA and MARTIN were much higher than those used by the present authors, the agreement does not seem to be unreasonable.

Further studies along these lines are in progress in this laboratory.

Acknowledgement—This investigation was made possible by support from the U.S. Atomic Energy Commission.

[16] B. C. PURKAYASTHA and G. W. MARTIN, *Canad. J. Chem.* **34**, 293 (1956).

J. Inorg. Nucl. Chem., 1960, Vol. 16, pp. 8 to 9. Pergamon Press Ltd. Printed in Northern Ireland

THE HALF-LIFE OF ANTIMONY-125*

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(*Received* 25 *March* 1960)

Abstract—The half-life of antimony-125 separated from uranium fission products has been determined to be 2·6 ± 0·1 years by measurements on a Lauritsen electroscope over a 5 year period.

Two distinct values for the half-life of antimony-125 are found in the literature, 2·7 and 2·0 years. The 2·7 year value is an early measurement determined by LEADER and SULLIVAN[1] during the Manhattan project by counting three samples with a mica window G–M tube over a period of half a year. The value of 2·0 ± 0·2 years is a more recent determination by LAZAR[2] obtained by measuring the areas under two peaks from γ-ray scintillation spectrometer tracings at two times which were one year apart. We have measured a sample of this nuclide regularly over a period of two half-lives, 5 years, in order to obtain a more accurate value of its half-life.

Fission product antimony was isolated from irradiated uranium which had stood about 3 years after removal from the reactor. The separation method involved two precipitations as the sulphide, extraction from a saturated oxalic acid solution into ethyl acetate, and final reduction to metallic antimony with chromous chloride. The finely divided metal was filtered and the sample was covered with a thin coat of paraffin wax.

Measurements were made with a Lauritsen electroscope in a modified housing[3] with aluminium foil windows of 3 mg/cm² thickness. A uranium standard was used for each measurement in order to correct the observed antimony activity for instrumental instability. This correction was always less than 3 per cent. The data are shown in Fig. 1. Measurements for Curve *A* were made with no added absorber and for Curve *B* with 35 mg/cm² of aluminium absorber over the sample. The lines shown are the result of least-square calculations which gave 2·69 ± 0·05 years for Curve *A* and 2·53 ± 0·05 years for *B*.

The possibility that these curves might be distorted by the 58 day ^{125m}Te daughter of ^{125}Sb was considered. This isomeric state decays by two γ-transitions of 110 and 35 keV energy, both highly internally converted.[2,4] The unconverted γ-radiation from these transitions involves about 7 per cent of the ^{125m}Te decays, and this isomer occurs in about 25 per cent of the ^{125}Sb decays so that less than 2 per cent of the total ^{125}Sb transitions give rise to a γ-ray in ^{125m}Te. The *L* and *M* conversion of the 110 keV transition produces the most energetic electrons from ^{125m}Te with an energy of about

* Contribution No. 870. Work was performed in the Ames Laboratory of the U.S.A.E.C.

[1] G. R. LEADER and W. H. SULLIVAN *Radio Chemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, DIV. IV, Vol. 9, p. 934. McGraw-Hill, New York (1951).
[2] N. H. LAZAR, *Phys. Rev.* **102**, 1058 (1956).
[3] A. F. VOIGT in F. M. UBER, *Biophysical Research Methods* Chap. 17, p. 613. Interscience, New York (1950).
[4] J. C. BOWE and P. AXEL, *Phys. Rev.* **85**, 858 (1952).

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105 keV. The range of electrons of this energy is 16 mg/cm². Since the sample was covered with at least 0·5 mm or 40 mg/cm² of wax, these electrons would not contribute to the rate of discharge of the electroscope. The efficiency of the electroscope for γ-radiation is only a few per cent of its efficiency for β-rays so that the ionization from the unconverted ^{125m}Te γ-rays would be well under 0·1 per cent of the contribution from ^{125}Sb betas. One would thus expect no observable effect on the decay curve from the growth of ^{125m}Te in the antimony sample.

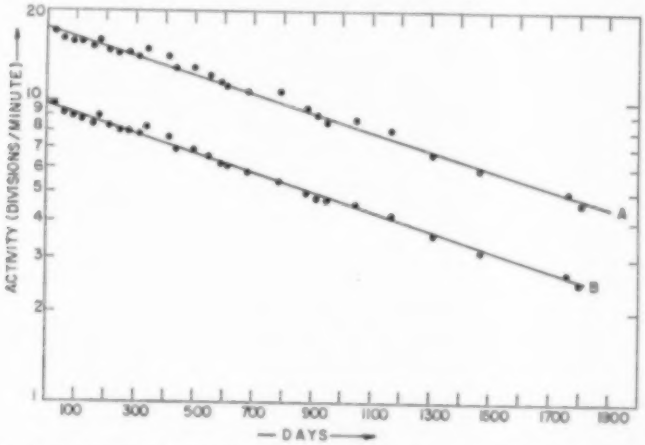

FIG. 1.—Decay curve of ^{125}Sb; Curve *A* is the decay curve with no added absorber, Curve *B* with 35 mg/cm² of Al absorber.

A γ-ray spectrum was taken on the sample at the end of the counting period using a 3 × 3 in. NaI (Tl) crystal and a 256 channel analyser (RCL Model 20611). Prominent peaks were obtained at 35, 120, 185, 455 and 637 keV in substantial agreement with results by LAZAR[2] and by SIEGBAHN and FORSLING[5]. The absence of other peaks is evidence of essential purity of the sample. A half-life of 2·6 ± 0·1 years is suggested as being consistent with these measurements.

[5] K. SIEGBAHN and W. FORSLING, *Arkiv Fysik* **1**, 505 (1949).

J. Inorg. Nucl. Chem., 1960, Vol. 16, pp. 10 to 15. Pergamon Press Ltd. Printed in Northern Ireland

NEW NEUTRON DEFICIENT ISOTOPES OF KRYPTON

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(*Received* 24 *May* 1960)

Abstract—Two new activities have been found in the neutron deficient isotopes of krypton produced by [*p*, *xn*] reactions on bromine. The half-lives have been determined as 12·0 ± 1·0 min and 5·5 ± 0·4 min. These activities are assigned to ^{74}Kr and ^{73}Kr respectively on the basis of their genetic relationships with bromine isotopes.

The isotope ^{74}Br has been observed to emit a positron with a maximum energy of 4·7 MeV and the half-life of this isotope is 25·7 ± 0·9 min.

THE lightest known isotope of krypton, ^{76}Kr, has a half-life of 9·7 hr[1] and the nucleus contains only two neutrons less than the stable ^{78}Kr (Fig. 1). Preliminary work in this Department by MORENO MORENO has indicated[2] that a more neutron deficient isotope with a short-life may exist. The unknown isotopes ^{73}Kr, ^{74}Kr and ^{75}Kr might have half-lives long enough to enable the decay to be followed using simple apparatus. We decided to attempt the production of new neutron deficient isotopes of krypton by bombarding lithium bromide targets with 280 MeV protons from the Liverpool Synchrocyclotron.

Kr 73 Short	Kr 74 12m	Kr 75 5·5m	Kr 76 9·7h	Kr 77 74m	Kr 78 Stable	Kr 79 34·5h	Kr 80 Stable	Kr 81 2×10^5y
Br 72	Br 73 4m	Br 74 26m	Br 75 1·6h	Br 76 16·3h	Br 77 57h	Br 78 6·4m	Br 79 Stable	Br 80 4·6h
Se 71 4·5m	Se 72 9·7d	Se 73 7·1h	Se 74 Stable	Se 75 127d	Se 76 Stable	Se 77 Stable	Se 78 Stable	Se 79 7×10^4y

FIG. 1.

EXPERIMENTAL

Fifty milligrammes of dry A.R. quality lithium bromide was sealed into a small thin walled silica target tube, which was then irradiated with a 1 μA beam of 280 MeV protons for 20 min.

The silica tube was broken inside a closed system to prevent leakage of the active gas, and dropped into boiling 2 M sodium hydroxide solution containing hold-back carriers for the appropriate spallation products. The liberated krypton was mixed with carbon dioxide as a carrier and was bubbled through a series of solutions containing oxidizing and reducing agents together with more hold-back carriers to remove gaseous impurities from the gas stream. At the end of the purification the carbon dioxide was absorbed by a solution of potassium hydroxide, thus leaving only a small volume of air containing the krypton. About 15 min elapsed between switching off the proton beam and having the pure gas ready for experiments.

* Present address: College of Technology, Liverpool, 3.

[1] A. A. CARRETTO and E. O. WIIG, *Phys. Rev.* **93**, 175 (1953).
[2] A. MORENO MORENO. Unpublished work.

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Counting techniques

A special counting apparatus was designed to follow the decay of the krypton gas and continually remove the decay products, so that the krypton decay curve is free from activities due to decay products. The krypton gas was contained in a thin-walled glass bulb mounted on a vertical glass stem. Periodically, sodium hydroxide solution could be pumped through a jet in the base of the glass stem so that the walls of the vessel were completely washed down. The wash liquor drained back into the stem and was returned to the circulating pump via a reservoir. The scalers recording the decay and the pump controlling the washing were operated by a time switch working on a six minute cycle. The counts from various detectors were recorded by the scalers for 5 min, the scalers were then switched off for 1 min, and the pump operated for 45 sec to wash out the decay products, the wash

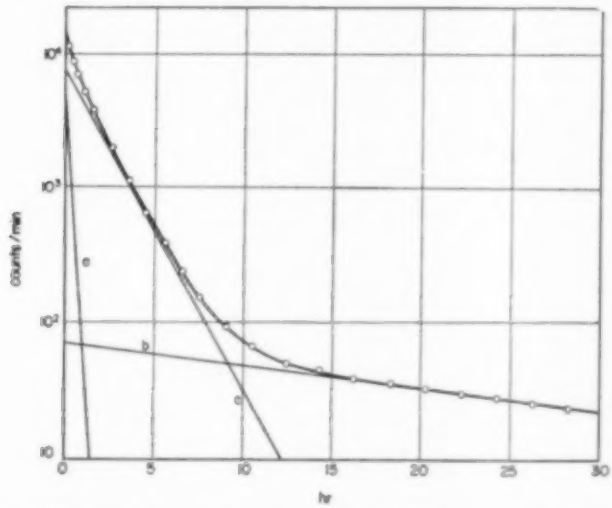

FIG. 2.—Decay of krypton isotopes. (a) 12 min. (b) approx. 20 hr. (c) 71 min.

liquor being allowed to drain before the next cycle commenced. The counts recorded by the scalers in each cycle were printed and the apparatus would work continuously for two weeks without attention.

Another apparatus was used to extract the bromine daughters of the active krypton at regular intervals, so that the decay of the krypton isotopes could also be observed using the "milking" technique.

RESULTS

A typical curve of the krypton produced by a [*p*, *xn*] reaction on a lithium bromide target is reproduced in Fig. 2. The decay curve shows three components, one with a half-life of 21 min, a main component of 1·1 hr due to ^{77}Kr[3,4,5,6] and a longer one of apparently about 20 hr which was shown, by a study of the γ-ray spectra, to be due to a mixture of ^{76}Kr and ^{79}Kr.

Krypton-77

The krypton produced in these bombardments always contained a large proportion of ^{77}Kr. The half-life of this isotope has been re-determined. In a series of

[3] L. L. WOODWARD, D. A. MCCOWN and M. L. POOL, *Phys. Rev.* **74**, 761 (1948).
[4] S. THULIN, *Arkiv. Fysik* **9**, 137 (1955).
[5] J. BEYDON, R. CHAIMINADE, M. CRUT, H. FARAGGI, J. OLKOWSKY and A. PAPINEAU, *Nucl. Phys.* **2**, 593 (1957).
[6] M. ATTERLING, J. BEYDON and J. OLKOWSKY, *Nucl. Phys.* **2**, 619 (1957).

six experiments the mean value was found to be 71·1 ± 0·5 min (standard deviation) which is slightly lower than the value reported by Thulin[4].

Kryptons with mass numbers less than 76

When a decay curve of krypton activities was analysed graphically, a short-lived component always remained after the long lived and 71 min activities had been subtracted from the total activity. The short lived component had a half-life of about 12 min with indications of an even shorter component having a half-life of about 5 min. These decays were attributed to new isotopes of krypton.

It was very difficult to examine the radiations from these short lived isotopes in the presence of intense radiations from the longer lived isotopes. Experiments designed

Table 1

Bromine daughter	Half-life	Krypton parent	Half-life
^{77}Br	57 hr	^{77}Kr	71 min
^{76}Br	16 hr	^{76}Kr	9·7 hr
^{75}Br	1·6 hr	^{75}Kr	unknown
^{74}Br?	26 min	^{74}Kr?	unknown

to improve the detection ratio, on a Geiger counter, of activities with half-lives longer than 12 min using aluminium absorbers up to a thickness of 500 mg/cm² were not successful.

The best values of the half-lives of these isotopes were established by milking the bromine daughters at regular time intervals. Discussion of these experiments will be deferred until the nature of the bromine decay products has been described.

The bromine decay products of the new krypton isotopes

Examination of the bromine decay products of the krypton showed that there were four isotopes involved. The results are shown in Table 1.

The bromine daughters of the known isotopes of krypton were found, together with ^{76}Br which must have been a decay product of one of the new isotopes of krypton. It was difficult to assign a mass number to the 26 min bromine activity. If it were due to the decay of ^{74}Br then the half-life conflicted with previously reported values of 36 min[7] and 42 ± 5 min.[5] The possibility that the 26 min activity was due to ^{73}Br was eliminated because the decay product ^{73}Se was not found in the decay products of krypton purified 25 min after irradiation.

The 26 min bromine isotope

This activity was not produced in useful quantities from spallation reactions (380 MeV protons) using target materials containing yttrium, strontium or rubidium. It is best obtained by allowing the krypton spallation products of [*p*, *xn*] reactions on bromine to decay for 5 min in contact with an alkaline solution containing bromide carrier and precipitating silver bromide. The range of the [presumed] positrons

[7] J. M. Hollander, *Phys. Rev.* **92**, 518 (1953).

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from the 26 min bromine activity was found to be 2·4 g/cm² in aluminium corresponding to a maximum energy of 4·7 MeV. This very energetic positron enabled the decay to be followed under favourable conditions. Aluminium foil of thickness 750 mg/cm² was sufficient to prevent low energy positrons from ^{75}Br and ^{77}Br reaching the Geiger counter. Fig. 3 shows a decay curve obtained in this way. The long tail is due to the 3·5 MeV positrons from ^{76}Br. This experiment shows quite clearly that the half-life of the bromine isotope is 26 min. Although the foils stopped positrons from ^{75}Br and ^{77}Br, the counter was still slightly sensitive to γ-radiations from these

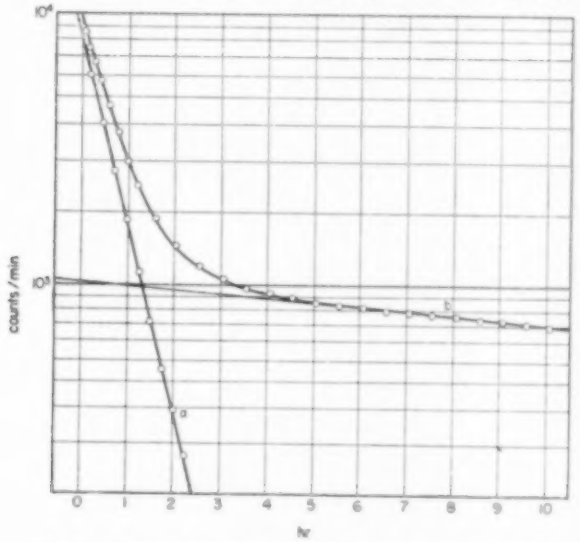

FIG. 3.—Decay of bromine isotopes. (a) 25·7 min. (b) 16·3 hr.

isotopes. The half-life of the short lived bromine was determined in a series of experiments in which the bromine activity was counted through an absorber thickness of 105 mg/cm² so that the positrons from ^{75}Br could be detected. The decay curves were then resolved into three components. The mean half-life of the short lived bromine isotope was 25·7 min, from twenty-one separate experiments (standard deviation 0·9 min).

γ-Spectrum of the 26 min bromine activity

It has been shown by TEMMER[8] and others[9] that ^{74}Se has a first excited state [2+] at 0·635 MeV above the ground state [0+]. The new bromine isotope was observed to emit a γ-ray of this energy which decayed with a half-life of 26 min. Further radiations with energies up to 3·1 MeV were observed but good statistical accuracy could not be achieved using the single channel pulse height analyser available. On this evidence and upon the fact that ^{73}Se is not observed we assign the 26 min bromine activity to ^{74}Br.

The half-life of ^{74}Kr

The half-life of ^{74}Kr was obtained by milking bromine from krypton at successive intervals of either 10 or 12 min and then finding the yield of ^{74}Br by examining the

[8] G. M. TEMMER and N. P. HEYDENBURG, *Phys. Rev.* **104**, 967 (1956).
[9] R. K. GIRGIS and R. VAN LIESHOUT, *Physica* **25**, 688 (1959).

decay curve of each bromine fraction counted through 750 mg/cm² of aluminium. The chemical recovery of the bromine from each fraction was found by comparing the amount of ^{76}Br produced from ^{76}Kr which has the much longer half-life of 9·7 hr. Fig. 4 shows the corrected yields of ^{74}Br plotted against time of separation. The half-life of ^{74}Kr based on ten experiments was 12·0 ± 1·0 min.

The half-life of ^{75}Kr

The half-life of ^{75}Kr was obtained using a similar technique but this time bromine was milked from krypton during successive 5 min periods. Each bromine fraction was

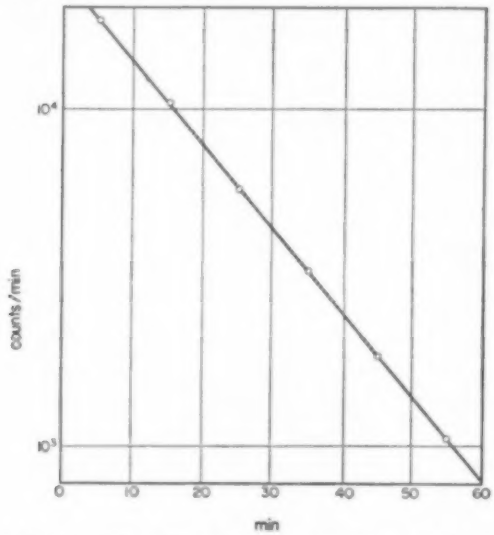

FIG. 4.—Yields of ^{74}Br milked from krypton at 12 min intervals.

counted through 105 mg/cm² of aluminium to stop the few positrons from ^{77}Br. The corrected yields of ^{75}Br are plotted against time in Fig. 5. The mean half-life of ^{75}Kr was 5·5 ± 0·4 min.

Bromine grown from 24 hr *old krypton*

Krypton which had been prepared for 24 hr was repurified and then bromine was allowed to grow for a further 12 hr. When this bromine was examined the only activity found was due to ^{76}Br. Thus there are no other long lived isotopes of krypton giving radioactive bromine daughters. The ^{76}Br obtained in this way was entirely free from other activities and the half-life could be determined accurately. Other workers have always determined the half-life from a source which was contaminated with other activities. Our value of 16·3 ± 0·3 hr may therefore be more reliable than the other reported values of 15·7 hr,[10] 17·2 hr[11] and 17·5 hr.[4]

Detection of a 4 min *bromine activity*

On one occasion a pure krypton fraction was obtained within 16 min of switching off the cyclotron beam. Bromine was milked from this krypton for 1 min, and the

[10] H. H. HOPKINS and B. B. CUNNINGHAM, *Phys. Rev.* **73**, 1406 (1948).
[11] S. G. FULTZ and M. L. POOL, *Phys, Rev.* **86**, 347 and 631 (1952).

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decay of the bromine fraction was being recorded 11 min later. When the decay curve was analysed the most abundant activity was due to ^{75}Br which had grown from the 5·5 min ^{75}Kr but there was also a short-lived activity with a half-life of 4 min. HOLLANDER[7] found that a 4 min activity was produced by bombarding ^{63}Cu with carbon ions and he assigned the activity to a bromine isotope with a mass number less than seventy-four. If our activity was due to a bromine isotope then the krypton

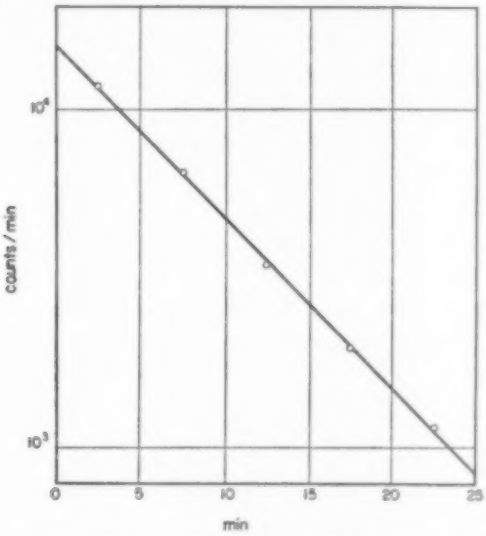

FIG. 5.—Yields of ^{75}Br milked from krypton at 5 min intervals.

parent must have a half-life longer than about 2 min. Further investigations on krypton isotopes of mass numbers less than seventy-four are being carried out. Until the results of these experiments are available this bromine activity and its krypton parent must be regarded as uncertain, for it is possible that the activity was due to contamination by ^{71}Se.

DISCUSSION

The assignment of the 12 min krypton activity to ^{74}Kr rests upon the assumption that the observed bromine daughter, which has a half-life of 26 min, is ^{74}Br. HOLLANDER[7] observed a 36 min activity in a bromine fraction produced by bombarding copper with 90 MeV carbon ions. The isotope was assigned to ^{74}Br on the basis of the relative yields from enriched ^{63}Cu and ^{65}Cu targets. BEYDON *et al.*[5] reported a γ-ray with a half-life of 42 ± 5 min. This radiation was also assigned to ^{74}Br. Apparently the 0·635 MeV γ-ray from the first excited state of ^{74}Se has been observed in both our research and in the work of BEYDON *et al.*, a strong indication that the assignment of the 26 min bromine activity to ^{74}Br is correct.

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THE THERMAL DECOMPOSITION OF IRRADIATED RUBIDIUM PERMANGANATE

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(*Received* 1 *March* 1960)

Abstract—The thermal decomposition of $RbMnO_4$, pre-irradiated in the spent fuel facility at Harwell and in a hollow uranium slug in BEPO, has been investigated in the temperature range 195°–245°. The results for γ-irradiated $RbMnO_4$ are similar to those for irradiated $AgMnO_4$ and $KMnO_4$ and the mechanism proposed for the latter is again suggested. The activation energy for the migration of point defects over the induction period is 1·59 eV. The p–t plots for pile irradiated $RbMnO_4$ are complex, and have been explained in terms of a mechanism involving the formation of thermal and/or displacement spikes.

PRE-IRRADIATION of crystals of $AgMnO_4$[1] and $KMnO_4$[2] by ^{60}Co γ-rays causes pronounced changes in the subsequent thermal decomposition in high vacuum. The characteristic changes are a shortening of the induction period, a decrease in the duration of the main acceleratory reaction, and an increase in the maximum velocity of reaction. The effects are explained by assuming that point defects are produced during irradiation and that these cationic defects are annealed at the decomposition temperature. The consequent formation of centres of decomposed material creates strain in the crystal lattice which causes fracture of the crystal. The onset of fracture marks the end of the induction period, after which reaction proceeds by the PROUT–TOMPKINS mechanism[3] of branching planes of reaction. A systematic study of the decomposition of pre-irradiated alkali metal permanganates should yield information as to the effect of varying the size and atomic weight of the cation involved. Consequently the decomposition of pre-irradiated $RbMnO_4$ was studied.

The thermal decomposition of unirradiated $RbMnO_4$ in the temperature range 215°–255° has been investigated.[4] The pressure–time plots for the decomposition of whole crystals resemble those for the decomposition of whole crystals of $KMnO_4$.[3] The "induction period" is a slow reaction during which the evolution of oxygen is linear with time. The acceleratory and decay periods follow the PROUT–TOMPKINS equation,[3]

$$\log [p/(p_f - p)] = kt + c \qquad (1)$$

if the origin is taken as the end of the induction period. The induction period is eliminated by grinding the crystals.

EXPERIMENTAL

The preparation of crystals of $RbMnO_4$ (2·5 mm × 0·5 mm), the apparatus and the procedure used were as previously described.[4] Whole crystals were ground to a fine powder in an agate mortar. Approximately 20 mg of whole and ground crystals were decomposed for a run. Normalization to a common final pressure was done for comparative purposes.

[1] E. G. PROUT and M. J. SOLE, *J. Inorg. Nucl. Chem.* **9**, 232 (1959).
[2] E. G. PROUT, *J. Inorg. Nucl. Chem.* **7**, 368 (1958).
[3] E. G. PROUT and F. C. TOMPKINS, *Trans. Faraday Soc.* **40**, 488 (1944).
[4] P. J. HERLEY and E. G. PROUT, *J. Phys. Chem.* **64**, 675 (1960).

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Pre-irradiation with γ-rays was performed in the spent fuel facility at Harwell. The dose rate was 4 Mrad hr^{-1}, and the samples were enclosed in sealed Pyrex glass ampoules. Irradiations were also carried out for one week at approximately 50° in a hollow uranium slug in BEPO. The approximate fluxes were: fast neutrons, 3×10^{11} neutrons cm^{-2} sec^{-1}; thermal neutrons, $1{\cdot}3 \times 10^{12}$ neutrons cm^{-2} sec^{-1}. The samples were contained in sealed silica ampoules and were decomposed two months after irradiation.

RESULTS

The decompositions at 220° of whole and ground crystals pre-irradiated by γ-rays (dose = 10 Mrad) were highly reproducible, since the p-t plots for three consecutive runs were, in each case, almost superimposable. No mass effect was found, k_1, k_2 and I

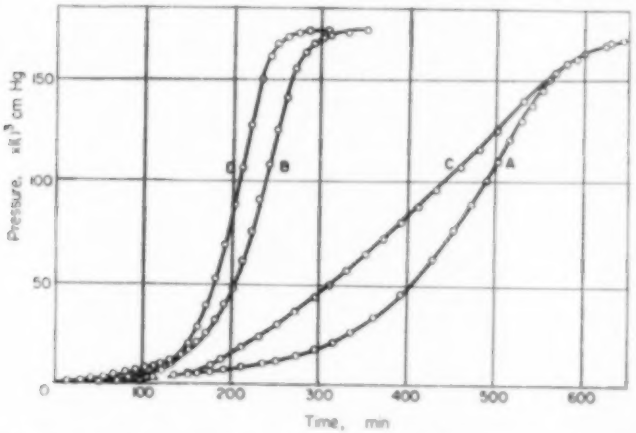

FIG. 1.—Effect of pre-irradiation by γ-rays on the thermal decomposition of whole crystals at 220°.
A—unirradiated whole crystals; B—whole crystals, 10 Mrad;
C—unirradiated ground crystals; D—ground crystals, 10 Mrad.

(see later) being independent of mass for a given dose and decomposition temperature. The effects of pre-irradiation in the γ-ray source on whole and ground crystals are illustrated in Fig. 1. The effect of pre-irradiation in the uranium slug is shown in Fig. 2.

The decomposition of γ-irradiated whole crystals (10 Mrad) was followed visually by withdrawing specimens at various times during a run and examining them microscopically. Fracture commenced at the end of the induction period and occurred throughout the acceleratory period. No fracture took place during the decay period. The final size of the particles varied between $1{\cdot}4 \times 10^{-3} - 1{\cdot}8 \times 10^{-4}$ cm. This is smaller than the corresponding value for unirradiated material (8×10^{-3} cm).

Figs. 2 and 3 illustrate the effects of varying the γ-ray dose for a fixed temperature of decomposition for whole and ground crystals respectively. As with pre-irradiated $AgMnO_4$ and $KMnO_4$ the length of the induction period varied with dosage according to the equation.

$$\log \tau = kI + c \qquad (2)$$

where τ = dose in Mrad, and I = length of the induction period. In contrast to unirradiated ground material pre-irradiated ground crystals show a period of slow reaction (the "induction period") which precedes the main acceleration of the reaction. The plots of log τ against I are shown in Fig. 4.

Interruption of the decomposition of unirradiated whole crystals after a definite time, irradiating in the γ-ray source for a constant dose and then continuing the decomposition was studied as for $KMnO_4$ and $AgMnO_4$. The results are shown in Fig. 5.

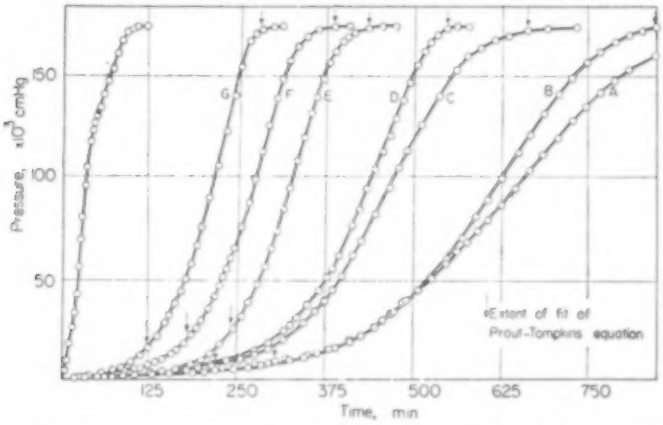

FIG. 2.—Effect on thermal decomposition of varying times of irradiation of whole crystals. Dose: A—0 Mrad; B—0·26 Mrad; C—1·2 Mrad; D—3·3 Mrad; E—10 Mrad; F—36 Mrad; G—106 Mrad; H—whole crystals pre-irradiated for one week in hollow uranium slug in BEPO.
Decomposition temperature, 220°.

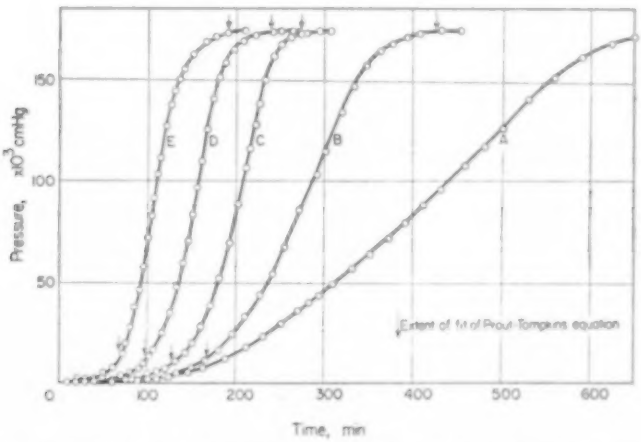

FIG. 3.—Effect on thermal decomposition of varying γ-ray dosage of ground crystals. Dose: A—0 Mrad; B—1·2 Mrad; C—10 Mrad; D—36 Mrad; E—106 Mrad.
Decomposition temperature, 220°.

The average percentage decomposition for unirradiated whole and ground crystals, calculated in terms of the equation

$$4RbMnO_4 \rightarrow 2Rb_2O + 4MnO_2 + 3O_2$$

and using the gaseous pressure of evolved oxygen, was 82·4. The corresponding average value for the decomposition of all γ-irradiated specimens was 82·7 per cent. In an attempt to detect any appreciable decomposition and the subsequent trapping of

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the generated oxygen during irradiation three separate runs were performed where the irradiated specimens (20 mg, 106 Mrad) were dissolved in hot water in a large decomposition bucket, evaporated over P_2O_5, in a desiccator, and then decomposed at 230°.

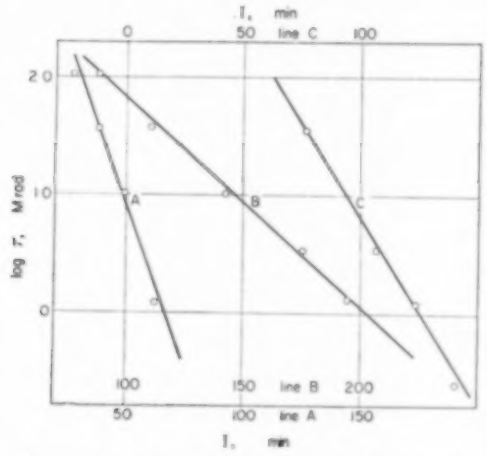

FIG. 4.—Relation between induction period (I) and irradiation dose (τ). A—whole crystals, decomposed at 230°; B—whole crystals, decomposed at 215°; C—ground crystals, decomposed at 220°.

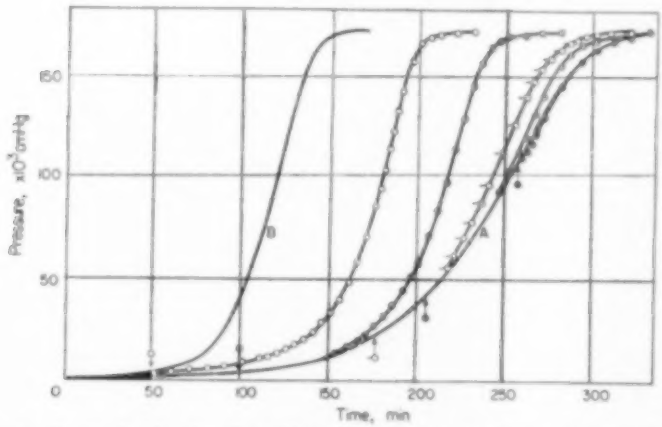

FIG. 5.—Curves showing the effect of interrupting a decomposition at time shown by appropriate arrow, irradiating in γ-ray source (dose, 9 Mrad), and then continuing decomposition with original $t = 0$ min.
Times of interruption as indicated by arrows: A—uninterrupted; B—0 min; ○—50 min; ①—100 min; ⟲—177 min; ⊖—205 min; ⊕—258 min.

No $RbMnO_4$ was lost during solution or evaporation. The average percentage decomposition was 82·0, indicating the absence of any experimentally determinable decomposition during irradiation.

The applicability of the Prout–Tompkins equation to the p-t plots of γ-irradiated whole and ground crystals was tested. In this the origin was transferred to the end of the induction period. Figs. 2 and 3 show that the equation describes the decay periods

of all decompositions and the acceleratory periods of the decomposition of whole crystals if the maximum velocity attained is less than the limiting value. The acceleratory periods of the decompositions of whole crystals pre-irradiated for doses greater than 10 Mrad, and the corresponding periods for ground crystals are partly represented by the equation. Activation energies were determined from the values of k (k_1 for the acceleratory period, k_2 for the decay period). The activation energies are tabulated in Table 1. The estimated accuracy for these values is 1·5 kcal/mole.

TABLE 1

Specimen	E_1 (kcal/mole)	E_2 (kcal/mole)
Whole crystals, 3·3 Mrad	41·5	38·2
Whole crystals, 10 Mrad	40·4	41·1
Whole crystals, 106 Mrad	41·5	41·0
Ground crystals, 10 Mrad	39·2	38·3

The plots log I vs. $1/T°K$ for whole and ground crystals for a fixed dose are straight lines (Fig. 6.) The activation energies calculated from the slopes are tabulated in Table 2.

The p–t plots for the decomposition of whole crystals pre-irradiated in the hollow slug are of a complex shape (Fig. 7) and differ considerably from those for γ-irradiated specimens. A series of decompositions at different temperatures was carried out. Microscopic observation of specimens withdrawn at various times (see Fig. 7)

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TABLE 2

Specimen	Activation energy (eV)
Whole crystals, 3·3 Mrad	1·50
Whole crystals, 10 Mrad	1·44
Whole crystals, 106 Mrad	1·64
Ground crystals, 10 Mrad	1·78
Mean	1·59

showed that disintegration commenced at $t \approx 9$ min and proceeded extremely rapidly until $t = 16$ min when the particle size was $\sim 2{\cdot}4 \times 10^{-3}$ cm. Thereafter, fracture took place at a slower rate and was complete at $t = 45$ min when the particle size was $\sim 1 \times 10^{-5}$ cm. The average percentage decomposition was 83·7.

DISCUSSION

The results for γ-irradiated whole and ground crystals are similar to those for pre-irradiated $KMnO_4$ and $AgMnO_4$, and consequently the mechanism proposed for the decomposition of these two substances is again suggested. The interaction of the γ-rays will occur principally by the Compton effect[5] and the crystals will be internally bombarded by fairly energetic electrons. Displacement of Rb^+ ions will occur by interaction with these electrons, producing primary knock-on atoms, with a few

[5] R. D. EVANS, *The Atomic Nucleus*. McGraw-Hill, New York (1955).

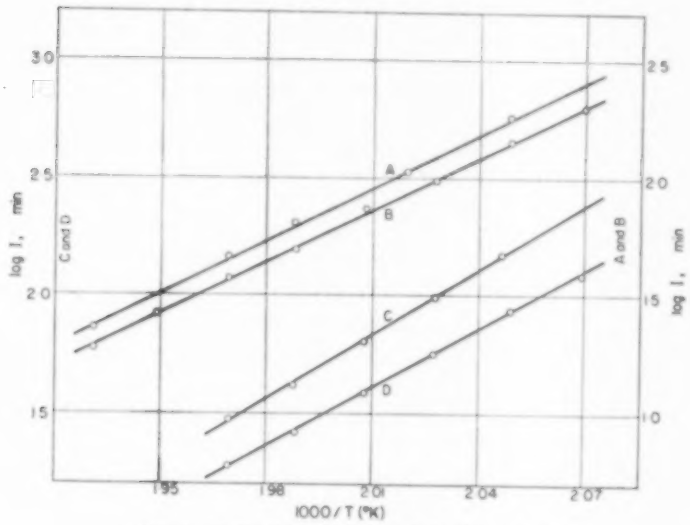

FIG. 6.—Activation energies for induction period.
A—whole crystals, 3·3 Mrad; B—whole crystals, 10 Mrad;
C—ground crystals, 10 Mrad; D—whole crystals, 106 Mrad.

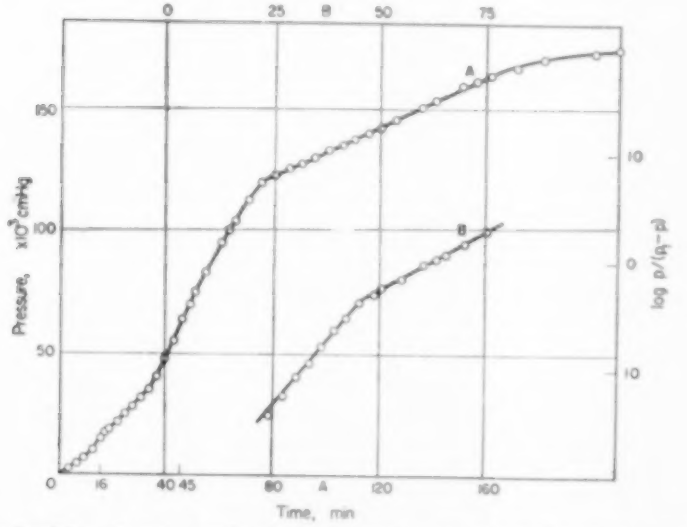

FIG. 7.—Effect of pre-irradiation of whole crystals for 1 week in hollow uranium slug.
A—pressure–time plot for decomposition at 205°; B—plot for Prout–Tompkins equation.

secondaries. The annealing of point defects and the creation of strain over the induction period will follow the pattern suggested for irradiated $KMnO_4$. The mean activation energy of 1·59 eV indicates the migration of vacancies over the induction period.

The results shown in Fig. 5 again indicate that different types of nuclei operate in unirradiated and irradiated material, although the delay phenomenon is not as well marked in the acceleratory period as with $KMnO_4$ and $AgMnO_4$. This is due to the

fact that the saturation maximum velocity, with increasing γ-ray dosage, is not sufficiently different from the maximum velocity of unirradiated material. As with $AgMnO_4$ and $KMnO_4$, interruption and irradiation in the decay period produces no effect. The "induction period" which occurs in the decomposition of γ-irradiated ground $RbMnO_4$ probably represents the growth of "irradiation nuclei" prior to fracture, and the "normal nuclei". It has been shown above that for whole crystals the acceleration of the decomposition by a reaction proceeding from irradiation nuclei is independent of the reaction originating from the nuclei ordinarily operative in unirradiated material.

Irradiation in a hollow uranium slug will produce atomic displacements as a result of fast neutron and γ-ray interaction. In addition, however, fast neutrons will produce thermal[6] and/or displacement[7] spikes. In $RbMnO_4$ these will not consist of centres of disorganised matter, but rather of decomposed material. Thus the centres which ultimately fracture the crystal will be preformed and of a greater density than in γ-irradiated material. At the decomposition temperature these will grow by an interface reaction similar to that occurring during the decay period. The early fracture, and initial rapid acceleration of the reaction to $t = 16$ min (Fig. 7), is probably associated with the rapid growth of these centres. After this rapid disintegration reaction should proceed by the Prout–Tompkins mechanism. If the origin is transferred to $t = 16$ min and the corresponding p value, it is found that the Prout–Tompkins equation is a good fit (Fig. 7), yielding two constants. The decay period, however, shows a discontinuity at $t \sim 75$ min after which the evolution of gas is almost linear with time. This is to be expected since the undecomposed fragments at this time will be extremely small and thus the evolution of gas at the small contracting reactant/product interface will be approximately linear with time. The plots of $\log k_1$, $\log k_2$ and $\log k_3$, against $1/T°K$, where k_1 and k_2 are the constants for the Prout–Tompkins equation, and k_3 the constant for the linear relationship, are well defined straight lines. Activation energies calculated from these plots are, $E_1 = 36{\cdot}5$, $E_2 = 40{\cdot}6$ and $E_3 = 38{\cdot}8$ kcal/mole. The estimated accuracy is 2 kcal/mole.

The activation energies for unirradiated whole crystals of $RbMnO_4$ are 39·5 and 40·2 kcal/mole for the acceleratory and decay periods respectively. The corresponding values for unirradiated ground crystals are 38·3 and 39·5 kcal/mole. The activation energies for irradiated $RbMnO_4$ are in close agreement with these values, indicating that the same chemical reaction occurs.

The high degree of reproducibility of results with pre-irradiated $KMnO_4$ and $RbMnO_4$, together with the relationship given by equation (2), suggest that the decomposition of irradiated material might form the basis of a radiation dosimeter.

Acknowledgement—The authors wish to thank the C.S.I.R.(S.A.) for a grant to cover the cost of irradiations and for a scholarship held by one of us (P. J. H.) during the investigation.

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J. Inorg. Nucl Chem., 1960, Vol. 16, pp. 23 to 28. Pergamon Press Ltd. Printed in Northern Ireland

PROTON MAGNETIC RESONANCE ABSORPTION IN FERROCENE AND ITS DERIVATIVES*

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(*Received* 1 *March* 1960)

Abstract—Broad-line proton magnetic resonance absorption lines for derivatives of ferrocene have higher second moments than those observed for ferrocene. This is interpreted in terms of the slowing-down of the motion of cyclopentadienyl rings resulting from substitution in one or both rings. The trend is found to depend on the size of the substituent, and to increase with substitution in both rings. Such substitution favours a freezing of motion more readily than in ferrocene itself, which gives a somewhat narrow line ($\delta H = 4$ Gauss) even at 77°K. Anomalous narrowing of absorption lines, observed in some cases at temperatures below room temperature, is discussed. Results of theoretical calculations of second moments for the rigid and motional models of ferrocene are presented. A comparison of these with the experimental values places the concept of rotation of rings in ferrocene on a sound basis.

FREE internal rotation of the cyclopentadiene rings in ferrocene is suggested by the electron diffraction pattern of its vapour,[4] by its infra-red and Raman spectra,[5] by measurements of dipole moment,[6,7] and by chemical studies.[8–11] X-Ray crystallographic studies[12–14] indicate that the rings occupy fixed staggered positions in the crystal, yet even here the apparent spreading of the carbon atoms along the circumference of the ring is regarded as being due possibly to hindered rotation of a fairly large amplitude. Molecular orbital calculations[12,15] have indicated no hindrance to the rotation of the rings. Such rotation would explain the absence of isomerism for the heteroannular derivatives of ferrocene. (The term heteroannular will be employed to designate derivatives of ferrocene in which both rings are monosubstituted.)

In the light of such evidence it is interesting to inquire into the nature of the molecular motion in ferrocene and its derivatives, in the crystalline state. Nuclear magnetic resonance studies[16] of crystalline substances have proven very useful in describing molecular motions of this sort, and have been used previously to support the concept

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[1] Dept. of Chemistry, University of Cincinnati, Cincinnati 21, Ohio.
[2] Dept. of Chemistry, University of Wisconsin, Madison, Wisconsin.
[3] Dept. of Chemistry, California Institute of Technology, Pasadena, California.

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of motion of cyclopentadienyl rings in ferrocene itself.[17] We now have undertaken a more detailed study of the proton magnetic resonance absorption of ferrocene and some of its derivatives, with special attention to comparative line widths and shapes.

EXPERIMENTAL

Proton magnetic resonance absorption was studied as a function of frequency at various temperatures by means of a Pound–Watkins type of radio-frequency spectrometer[18] and some auxiliary equipment which has been described previously.[19] A modulation frequency of 280 c/s was used. Absorption occurred in the neighbourhood of 17·8 mc, and the radiofrequency signal was monitored at roughly equal intervals of time by a BC-221 frequency meter. Saturation effects were avoided by using the lowest possible radiofrequency level, and low values of modulation (about a tenth of the line width) were used to prevent distortion of line shape. From the resulting derivative curves, the line width (δH, the frequency interval between points of extreme slope of the absorption curve) was measured and the second moment (ΔH_2^2) was calculated.

RESULTS AND DISCUSSION

Ferrocene

Before interpreting the results for ferrocene, it is necessary to estimate the effect of various motions on the second moment of the proton magnetic resonance absorption. The crystal structure of the substance is well known.[12–14] The inter-proton distances are shown in Fig. 1. From this information it is formally possible to calculate

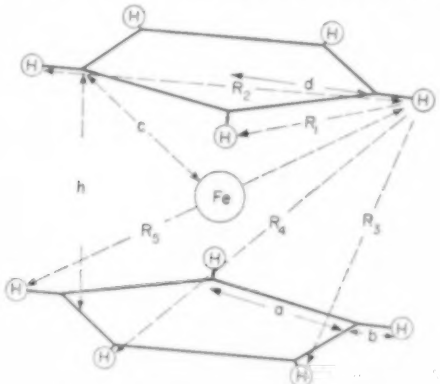

FIG. 1.—Proton interactions in ferrocene.
$R_1 = 2{\cdot}676$ Å, $R_2 = 4{\cdot}330$ Å, $R_3 = 3{\cdot}606$ Å, $R_4 = 4{\cdot}958$ Å, $R_5 = 5{\cdot}636$ Å.

ΔH_2^2 quite exactly for any particular state of motion by use of the theory of VAN VLECK[20] (as modified by POWLES and GUTOWSKY[21] and others). However, in this instance the protons are rather evenly distributed throughout the lattice, so that each proton has a rather large number of near neighbours. Coupled with the inherent complexity of handling motions in which the internuclear distance changes, this fact has required us to defer the exact solution until some later date. It is hoped that it will prove sufficient for the present to quote the following simplified calculations and to choose the most appropriate values: for isolated ferrocene molecules (i.e. no

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[21] J. G. POWLES and H. S. GUTOWSKY, *J. Chem. Phys.* **21**, 1695 (1953); *Ibid.* **23**, 1692 (1955).

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intermolecular interactions), rigidly fixed in a crystal lattice but randomly oriented as in a crystal powder, the VAN VLECK treatment yields $\Delta H_2^2 = 2{\cdot}4$ Gauss^2 as the expected second moment. Following the treatment of POWLES and GUTOWSKY[21] to estimate ΔH_2^2 for a similarly isolated ferrocene molecule rotating rigidly (without internal rotation) about the 5-fold axis of symmetry yields a value of 0·7 Gauss^2. Based on the known crystal structure,[7] ΔH_2^2 for a ferrocene crystal powder in the absence of any motion has been calculated[22] to be 8 Gauss^2. Our very rough estimate of the magnitude of the contributions of the intermolecular interactions to ΔH_2^2 for the rotating case suggests that about 1·5–2·5 Gauss^2 are to be added to the single-molecule calculation, giving a rough estimate of 2–3·5 Gauss^2 for a ferrocene crystal powder in which rotation is taking place about the 5-fold symmetry axis. The presence or absence of internal rotation is expected to have an effect of less than 0·5 Gauss^2 on this figure, and is therefore not distinguishable. Rotation about any other single axis is expected to give approximately the same value as for rotation about the symmetry axis, since the protons in the ferrocene molecule are distributed roughly uniformly over a sphere. For a situation in which the ferrocene molecules are assumed to be reorienting about *all* axes, the intramolecular contributions would be expected to average to zero. As before, we have estimated very roughly that the intermolecular contributions for this case should give a ΔH_2^2 of about 1–2 Gauss^2. The estimate of the intermolecular contributions given above for the various motions are based on the method of POWLES and GUTOWSKY[21], but the procedure used to obtain the necessary time averages was only approximate.

Proton magnetic resonance absorption in ferrocene was observed at several temperatures, and ΔH_2^2 was determined for some of these. The data are given in Table 1, along with a summary of the theoretical figures given above. The value of δH is calculated for Gaussian lines, i.e. $\delta H = 2(\Delta H_2^2)^{1/2}$.

TABLE 1.—COMPARISON OF THEORETICAL AND EXPERIMENTAL SECOND MOMENTS AND LINE WIDTHS FOR A FERROCENE CRYSTAL POWDER

Theoretical	ΔH_2^2 (Gauss^2)	δH (Gauss)
Calculated—no motion	8	5·7
Estimated—rotation about 5-fold symmetry axis (with or without internal rotation)	2–3·5	2·8–3·7
Estimated—free reorientation about all axes	1–2	2–2·8
Experimental (°K)		
298	2·8 ± 0·5	4·0
194	1·4 ± 0·5	2·2
77	5 + 0·5	4·0
63	—	~7·0
4	—	broad

If we disregard for the moment the values at 194°K, these data are rather easily interpreted. The observed ΔH_2^2 at 298°K is within the range of values suggested for rotation about the 5-fold axis. In view of the reported crystal structure,[7] this seems to be the most probable axis of rotation. Since the Fourier density map of the unit

cell shows not only the two cyclopentadiene rings rather clearly, but also identifies the location of the carbon atoms in each ring to some extent, we can only say that this motion is probably of the nature of a hindered rotation or jumping between positions of equilibrium. Large-amplitude oscillation without jumping would not be expected to be a motion sufficient to produce so narrow a line.

The problem of internal rotation cannot be decided on the basis of the present evidence. The observations at 77°K and below give indication that this motion may be frozen out at sufficiently low temperatures, and a transition seems to occur in the general vicinity of 77°K. According to the theory of POWLES and GUTOWSKY, the rate of motion in this region is of the order of the line width expressed in frequency units ($\sim 2 \times 10^4$ sec^{-1}). It would be very interesting to be able to determine the manner in which this motion does freeze out, assuming that both overall rotation and internal rotation are occurring above this region; but unfortunately it is not possible to say.

The value at 194°K is difficult to account for except in terms of saturation. HOLM and IBERS[22] report that in this temperature region ΔH_2^2 is essentially constant, with a value the same as that at room temperature, but that the spin-lattice relaxation time, T_1, varies over a large range.[23] It is possible that a large number of interactions of different kinds in the ferrocene crystal produce a situation in which T_1, varies widely over the entire absorption line. This would account for the fact that in these observations the usual test for saturation (reducing the radiofrequency power level) gave no appreciable change in the appearance of the resultant absorption line, while the very low power levels used by HOLM and IBERS revealed an absorption of a considerably different character. These observations are supported to some extent by the observation that the discrepancies between δH and ΔH_2^2 are indicative of some complexity in the line shapes, possibly of the same origin as the complex T_1 dependence. There is also the possibility that solid-phase transitions may be present, multiplying the complexity of this situation.

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Derivatives of ferrocene

The statements made at the beginning of the previous section may be expected to apply to the derivatives of ferrocene also, with some qualifications. Only a limited number of derivatives have been studied for their crystal structure.[24,25] The crystal structures of some of the heteroannular derivatives are unknown, and these may be quite different from that of ferrocene. This is indicated by the fact that the densities of the derivatives are not very similar to that of ferrocene. In general, this will affect the size of the intermolecular contributions to ΔH_2^2; it makes uncertain the calculated value of ΔH_2^2 in the absence of motion, and doubly uncertain the values estimated for the cases in which motion is present. Second, the addition of substituents to the cyclopentadiene rings opens up the possibility of a variety of motions intermediate between no rotation and free rotation about a single axis. If one ring is tied down and the other is free to rotate, then a distinctly intermediate value of ΔH_2^2 is to be

[22] C. H. HOLM and H. A. IBERS, *J. Chem. Phys.* **26**, 1753 (1957); *Ibid.* **30**, 885 (1959). We wish to thank Dr. HOLM for sending us this and other information prior to publication.
[23] Dr. HOLM[22] has confirmed the observation of a similar reduction in ΔH_2^2, but also reports that he was able to eliminate it by going to very low power levels.
[24] T. L. KHOTSYANOVA, *Kristallografiya* **2**, 382 (1957).
[25] YU. T. STRUCHKOV, *Zh. Obshchei Khim.* **27**, 2039 (1957); *Dokl. Akad. Nauk SSSR* **110**, 67 (1956).

expected. Incomplete knowledge of the crystal structure makes cases of this sort especially difficult to estimate with any accuracy. Further, there are no definite reasons to expect that the most probable mode of motion is about the 5-fold axis of the ferrocene skeleton. Lastly, the protons occurring in the substituent groups themselves represent an additional unknown quantity. Depending upon the situation, such groups might result in anything from a net increase in the observed δH and ΔH_2^2 (if they are relatively stationary) to a net decrease (if they are relatively mobile and isolated from the other protons).[28]

TABLE 2.—LINE WIDTHS AND SECOND MOMENTS FOR PROTON RESONANCE ABSORPTION OF FERROCENE DERIVATIVES

Compound m.p. (°C)	Temperature (°K)	ΔH_2^2 (Gauss^2)	δH (Gauss)
Acetyl ferrocene,	298	4·6	2·8
89–90°	194	6·0	3·0
	77	6·0	8·8
1:1′ diacetyl ferrocene,	298	9·3	7·0
130–131°	194	9·6	7·0
	77	9·6	8·0
Benzoyl ferrocene,	298	9·0	2·4
108–109°	194	5·3	2·4
	77	10·0	9·7
Anilide of ferrocene	298	8·5	1·0
carboxylic acid,	77	9·4	9·4
205–207°			
1:1′(α-keto trimethylene)-	298	12·7	9·0*
ferrocene, 141–142°	194	13·0	9·2*
	77	14·5	9·2

* A narrow component superimposed on the broad line was observed.

Table 2 lists the results for the various derivatives of ferrocene, δH and ΔH_2^2 being defined as before. The melting points of the several compounds also are indicated.

Considering the second moments in Table 2, we find that at 298°K acetyl ferrocene is the only compound which exhibits any great amount of motion. More than likely the free ring is moving somewhat more than the unsubstituted one. It is possible that a substituent of the size of the acetyl group may not suppress completely the motion of the other ring, but it would be expected to reduce it to some sort of eccentric motion. As far as one may guess, the value of ΔH_2^2 is about right for such a motion. At 194°K and at 77°K this motion is partially or wholly frozen out. Possibly the unsubstituted ring is still free to move somewhat, even at the lowest temperature. Although the other compounds do show some tendency for an increased ΔH_2^2 at lower temperatures, there are no indications that any motions of large amplitude are taking place. It may be asked why benzoyl ferrocene and the anilide of ferrocene carboxylic acid do not have narrower lines than they do, for without taking into account the differences between the crystalline environments, it would seem that here again one ring should be free and one fixed, resulting in a ΔH_2^2 only slightly greater than that for acetyl ferrocene. In answer to this question, it can only be pointed out that in acetyl ferrocene the motion

[28] Work is currently under way at the University of Cincinnati to prepare for study some derivatives containing non-protonated substituents, such as perdeutero and perfluoro groups, in an attempt to avoid this difficulty.

seemed to be frozen out at some temperature intermediate between 298°K and 194°K. Only a slight difference between the crystal structures of these compounds or the roles of the substituents is necessary to cause the freezing out to occur at some temperature above 298°K. Quite possibly the heavier substituent restricts the freedom of the other ring as well as that of its own, especially if the parallel arrangement of the rings were to become distorted.[27] It is significant that the broadest lines recorded were those for 1 : 1′ α-keto trimethylene-ferrocene, in which a $-CH_2-CH_2-\underset{|}{C}:O$ bridge joins the two rings and precludes the possibility of independent motion. This may be considered to be the compound most likely to rotate about axes other than those near the 5-fold axis of the ferrocene skeleton. Apparently neither this motion nor rigid rotation about the 5-fold axis occurs.

The values for line width, insofar as they can give any indication of the line shape, are somewhat more interesting and also somewhat more uncertain for these substituted compounds. It may be seen that there is no really close correspondence between line width and second moment. This may be due partly to the peculiarities of line shape suggested in the discussion of ferrocene, or it may be due to the more mundane possibility that the several different kinds of protons (i.e. ring protons vs. substituent protons) each contribute a different simple line shape to make up the resultant complex line shape. It also is possible that these compounds, which are somewhat difficult to procure in sufficient quantity for adequate purification may have possessed sufficient impurity (possibly solvent of crystallization) to contribute a net distortion of the apparent line shape, and correspondingly to affect δH without appreciably affecting ΔH_2^2.

CONCLUSIONS

A comparison of the observed second moments for proton magnetic resonance absorption for ferrocene with theoretically estimated values supports the concept of free rotation of cyclopentadiene rings in ferrocene. Substituting various organic groups for hydrogen in one or both rings results in a restriction of such motion and in a broadening of the absorption lines. In "bridged" ferrocene the possibility of free rotation of the rings is precluded, and this situation gives rise to the extremely broad lines expected of solids in which there is little or no motion at all.

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[27] Such tilting without affecting stability is feasible. A bridged ferrocene with a two-carbon-atom bridge, in which the cyclopentadiene rings are definitely tilted, has been reported by Dr. ROY L. PRUETT of Union Carbide Chemical Company.

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VAPOUR EQUILIBRIA IN THE B_2O_3–H_2O SYSTEM AT ELEVATED TEMPERATURES

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Abstract—The equilibrium pressures of $H_3BO_{3(g)}$, $HBO_{2(g)}$ and $(HBO_2)_{3(g)}$ have been determined by a transpiration method in the temperature region 1000°–1273°K. From these data, the calculated heats of formation are:

$$\Delta H_{f_{0°K}}\,[HBO_{2(g)}] = -134{\cdot}9 \pm 1 \text{ kcal/mole, and}$$

$$\Delta H_{f_{0°K}}\,[(HBO_2)_{3(g)}] = -537{\cdot}5 \pm 3 \text{ kcal/mole.}$$

THE existence of gaseous hydroxides of boron has been known for many years STACKELBERG and co-workers[1] observed the sublimation of H_3BO_3 and determined the heat of formation of the gas. MARGRAVE and DAMRON[2] postulated that $HBO_{2(g)}$ was a significant species in water vapour over B_2O_3 in the 500°–900°C range from studies of log P_{H_2O} vs. log P (boron species) curves, the slopes of which deviated from that expected for $H_3BO_{3(g)}$. Further work of this type reported by MARGRAVE *et al.*[3] could not be reconciled with the assumption that a single species, either $H_3BO_{3(g)}$ or $HBO_{2(g)}$, was present, since the slope of the log–log plots was observed to be approximately unity in the temperature and water vapour-pressure region studied. Some deviations from this slope were noted, but at first were believed to be within the order of experimental error.

The recent work of CHUPKA and BERKOWITZ[4] has aided materially in clarifying the gaseous boron hydroxide problem. In mass spectrographic studies of the reaction of B_2O_3 with water vapour at 1250°C, these investigators observed the presence of $H_3BO_{3(g)}$, $HBO_{2(g)}$ and a third boron hydroxide species; the trimer, $(HBO_2)_{3(g)}$.

WHITE *et al.*[5] have observed the infrared spectrum of gaseous HBO_2 from which they have calculated reliable thermal functions for the gas. Also, by observing the variation in emission intensity of an $HBO_{2(g)}$ vibrational band as a function of temperature, WHITE *et al.*[5] determined the heat of formation of the gas as $\Delta H_{f_{0°K}} = -135{\cdot}0 \pm 2{\cdot}5$ kcal/mole. These investigators also calculated thermal functions for $(HBO_2)_{3(g)}$ with certain assumptions about the structure of the molecule and estimation of the fundamental vibrational frequencies. A heat of formation of -537 ± 10 kcal/mole was assigned to the trimer.[6]

[1] M. VON STACKELBERG, F. QUATRAM and J. DRESSEL, *Z. Elektrochem.* **43**, 14 (1937).
[2] J. L. MARGRAVE, *J. Phys. Chem.* **60**, 715 (1956).
[3] J. L. MARGRAVE, J. R. SOULEN, G. E. LEROI, F. T. GREENE and S. P. RANDALL, *Memoirs of the Inorganic Section, XVIth International Congress of Pure and Applied Chemistry, Paris*, pp. 521–527 (1957).
[4] W. A. CHUPKA and J. BERKOWITZ, Abstracts of the 135th Meeting of the American Chemical Society, Boston, Massachusetts, April, 1959; *J. Chem. Phys.* **33**, 530 (1960).
[5] D. WHITE, D. E. MANN, P. N. WALSH and A. SOMMER, Technical Report No. 3, Contract Nonr-495(12), between the Ohio State University Research Foundation and the Office of Naval Research, June, 1959; *J. Chem. Phys.* **32**, 488 (1960).
[6] D. WHITE, P. N. WALSH, D. E. MANN and A. SOMMER, Technical Report No. 4, Contract Nonr-495(12), between the Ohio State University Research Foundation and the Office of Naval Research, July, 1959; *Proceedings of the Propellant Thermodynamics and Handling Conference*, American Rocket Society, Ohio State University, Columbus, Ohio, July, 1959.

The present work is the result of investigations of the $B_2O_{3(l)}$–$H_2O_{(g)}$ system using the transpiration method in an effort to determine the equilibrium pressures of the various boron hydroxide species present. Preliminary results were presented at a recent American Rocket Society meeting.[7]

EXPERIMENTAL

Flow measurements were carried out in a Vycor tube, 25 mm i.d., placed in a nichrome wound resistance furnace. One end of the tube was sealed off except for a small Vycor tube down the centre of the larger tube which had a small hole (2 mm dia.) pointing directly downward at the end. B_2O_3 in a large flat platinum boat was placed beneath the hole in this Vycor inlet tube and mixtures of H_2O vapour and N_2 flow gas were allowed to impinge directly upon the surface of the liquid B_2O_3 in the boat. The temperature of the B_2O_3 was controlled to $\pm 5°C$ by means of a chromel P–alumel thermocouple and Amplitrol.

The mixing of the H_2O vapour and nitrogen flow gas was accomplished by passing known quantities of nitrogen gas (measured by a calibrated flowmeter) through a fritted glass tube submerged in distilled water of accurately known temperatures. Once saturated, the moisture-containing nitrogen gas was passed through heated Pyrex tubing leading to the furnace chamber to prevent any loss of water vapour by condensation.

The flow rate was varied by adjusting the flow velocity of the nitrogen gas, and the water vapour partial pressure was controlled by adjusting the temperature of the water in the saturator. The duration of each flow run was measured from the time of placing the boat into the furnace to the time of removal. The boat was kept in a desiccator and accurately weighed before and after each run. The weight loss of B_2O_3 from each run was ascribed to the formation of gaseous boron hydroxides. No measurable weight loss of B_2O_3 occurred under a dry nitrogen flow gas at these temperatures. In most cases, the time of the flow run was of sufficient length (ca. 1 hr) that the error introduced by the time required to bring the boat up to furnace temperature was kept small.

Without any assumptions about the exact mixture of the vapour species one may define the pressure of gaseous boron species as

$$P_b = 2\left(\frac{n_{B_2O_3}/t}{n_{total}/t}\right)P_{total}$$

where $(n_{B_2O_3}/t)$ = moles of B_2O_3 lost per unit time from the boat on passing (n_{total}/t) moles of gas per unit time over the boat under a total pressure P atmospheres and the two takes account of the fact that there are two boron atoms per B_2O_3 formula unit.

It was difficult to achieve equilibrium conditions in the furnace chamber at any finite flow rate. In an effort to establish the general shape of the curves for $\log P_{H_2O}$ vs. $\log P_b$, flow runs were carried out at a low, constant nitrogen flow rate and variable water vapour pressure at two fixed temperatures (1073°K and 1273°K). The results of these two series of runs are given in Tables 1 and 2.

Although the flow rate of nitrogen gas through the system was maintained constant for these runs, the total number of moles of nitrogen gas plus water vapour per unit time was not a constant. P_b' is the total boron species pressure for each flow run corrected to a constant total number of moles of N_2 plus H_2O of $2{\cdot}0 \times 10^{-1}$ mole/hr. These corrections were based on numerous observations that at the temperatures considered and at the water vapour pressure and flow rate regions studied in Tables 1 and 2, an inverse and approximately linear relationship exists between the flow rate and the determined total boron species pressure. The logs of these corrected, non-equilibrium pressures vs. the log of the water vapour pressure are shown by the lower curves in Figs. 1 and 2. These curves are expected to be parallel to the equilibrium curves, and thus may be used to establish the slopes for the $\log P_b$ vs. $\log P_{H_2O}$ equilibrium plots.

In order to obtain equilibrium (saturation) values for the total vapour-pressure of the boron hydroxide species present, it was necessary—at a fixed temperature and water vapour pressure—to make a series of flow runs at progressively lower flow rates and to extrapolate to zero flow rate. This method did not, immediately, give a satisfactory value for the equilibrium pressure because of

[7] L. H. SPINAR, S. P. RANDALL, F. T. GREENE and J. L. MARGRAVE, *Proceedings of the Propellant Thermodynamics and Handling Conference*, American Rocket Society, Ohio State University, Columbus, Ohio, July, 1959.

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diffusion loss effects. Diffusion loss corrections were therefore applied following the method of TOMBS and WELCH[8] with one further modification. It was found that the weight loss of B_2O_3 in an initially measured water vapour atmosphere and zero flow rate was not a linear function of the time that the boat was in the furnace. Rather, it was found that the weight loss was proportionally higher the shorter the time that the boat was allowed to remain in the furnace.

TABLE 1.—NON-EQUILIBRIUM TOTAL PRESSURES OF GASEOUS BORON HYDROXIDES
$T = 1073°K$

Flow Run	$P\,H_2O$ (atm)	N_2 Flow (mole/hr)	H_2O Flow (mole/hr)	P_b (atm)	P_b' atm.
1·4	$3{\cdot}12 \times 10^{-2}$	$19{\cdot}3 \times 10^{-3}$	$0{\cdot}62 \times 10^{-2}$	$0{\cdot}21 \times 10^{-3}$	$0{\cdot}21 \times 10^{-3}$
2·4	$8{\cdot}52 \times 10^{-2}$	$19{\cdot}3 \times 10^{-3}$	$1{\cdot}69 \times 10^{-2}$	$0{\cdot}82 \times 10^{-3}$	$0{\cdot}86 \times 10^{-3}$
3·4	$1{\cdot}65 \times 10^{-1}$	$19{\cdot}3 \times 10^{-3}$	$3{\cdot}22 \times 10^{-2}$	$2{\cdot}02 \times 10^{-3}$	$2{\cdot}28 \times 10^{-3}$
4·4	$2{\cdot}58 \times 10^{-1}$	$19{\cdot}3 \times 10^{-3}$	$5{\cdot}11 \times 10^{-2}$	$2{\cdot}84 \times 10^{-3}$	$3{\cdot}46 \times 10^{-3}$
5·4	$3{\cdot}96 \times 10^{-1}$	$19{\cdot}3 \times 10^{-3}$	$7{\cdot}77 \times 10^{-2}$	$4{\cdot}36 \times 10^{-3}$	$5{\cdot}92 \times 10^{-3}$

TABLE 2.—NON-EQUILIBRIUM TOTAL PRESSURES OF GASEOUS BORON HYDROXIDES
$T = 1273°K$

Flow run	$P\,H_2O$ (atm)	N_2 flow (mole/hr)	H_2O flow (mole/hr)	P_b (atm)	P_b (atm)
1·3	$8{\cdot}52 \times 10^{-2}$	$19{\cdot}3 \times 10^{-3}$	$1{\cdot}69 \times 10^{-2}$	$1{\cdot}11 \times 10^{-3}$	$1{\cdot}16 \times 10^{-3}$
2·3	$1{\cdot}65 \times 10^{-1}$	$19{\cdot}3 \times 10^{-3}$	$3{\cdot}22 \times 10^{-2}$	$1{\cdot}95 \times 10^{-3}$	$2{\cdot}20 \times 10^{-3}$
3·3	$2{\cdot}58 \times 10^{-1}$	$19{\cdot}3 \times 10^{-3}$	$5{\cdot}11 \times 10^{-2}$	$3{\cdot}38 \times 10^{-3}$	$4{\cdot}12 \times 10^{-3}$
4·3	$3{\cdot}12 \times 10^{-2}$	$19{\cdot}3 \times 10^{-3}$	$0{\cdot}62 \times 10^{-2}$	$0{\cdot}55 \times 10^{-3}$	$0{\cdot}55 \times 10^{-3}$
5·3	$3{\cdot}96 \times 10^{-1}$	$19{\cdot}3 \times 10^{-3}$	$7{\cdot}77 \times 10^{-2}$	$4{\cdot}68 \times 10^{-3}$	$6{\cdot}34 \times 10^{-3}$

This effect was most probably due to the decrease in water vapour concentration in the furnace chamber at zero flow rate by diffusion out of the system, thus reducing the rate of formation of the gaseous hydroxides with time. Since during a normal flow run with a finite flow rate, the water vapour concentration was maintained constant over the B_2O_3 in the boat by the continuous influx of new flow gas, it was necessary to obtain the diffusion loss at zero flow rate under the same conditions of constant water vapour concentration. This was done by measuring the diffusion loss at a certain initial water vapour concentration at zero flow rate for different residual times of the boat in the furnace and extrapolating this weight loss per unit time to zero time of heating in the furnace.

The results of a number of series of flow runs performed as described above to determine the total equilibrium vapour pressure of the boron hydroxides present at various water vapour pressures and several different temperatures are given in Table 3. These equilibrium pressure values are also shown by the points on the upper curves in Figs. 1 and 2.

TABLE 3.—EQUILIBRIUM TOTAL PRESSURES OF GASEOUS BORON HYDROXIDES

Series no.	$T(°K)$	P_{H_2O}(atm)	P_b(atm)
0·11	1000	$1{\cdot}97 \times 10^{-1}$	$3{\cdot}84 \times 10^{-3}$
0·14	1100	$1{\cdot}97 \times 10^{-1}$	$4{\cdot}32 \times 10^{-3}$
0·8	1273	$9{\cdot}95 \times 10^{-2}$	$2{\cdot}30 \times 10^{-3}$
0·20	1273	$1{\cdot}97 \times 10^{-1}$	$4{\cdot}75 \times 10^{-3}$
0·9	1273	$3{\cdot}96 \times 10^{-1}$	$12{\cdot}0 \times 10^{-3}$

[8] N. C. TOMBS and A. J. E. WELCH, *J. Iron St. Inst.* **172**, 69–78 (1952).

DISCUSSION

If one assumes that $H_3BO_{3(g)}$, $HBO_{2(g)}$ and $(HBO_2)_{3(g)}$ are the important species from the reaction between water vapour and liquid B_2O_3 in the temperature range from 1000°K to 1300°K, one may write:

$$B_2O_{3(l)} + 3H_2O_{(g)} = 2H_3BO_{3(g)} \tag{1}$$

$$K_{p_1} = \frac{p^2_{H_3BO_3}}{p^3_{H_2O}}\ ;\ p_{H_3BO_3} = K^{1/2}_{p_1}\, p^{3/2}_{H_2O} \tag{1'}$$

$$B_2O_{3(l)} + H_2O_{(g)} = 2HBO_{2(g)} \tag{2}$$

$$K_{p_2} = \frac{p^2_{HBO_2}}{p_{H_2O}}\ ;\ p_{HBO_2} = K^{1/2}_{p_2}\, p^{1/2}_{H_2O} \tag{2'}$$

$$3B_2O_{3(l)} + 3H_2O_{(g)} = 2(HBO_2)_{3(g)} \tag{3}$$

$$K_{p_3} = \frac{p^2_{(HBO_2)_3}}{p^3_{H_2O}}\ ;\ p_{(HBO_2)_3} = K^{1/2}_{p_3}\, p^{3/2}_{H_2O} \tag{3'}$$

$$2n_{B_2O_3}/t = n_{H_3BO_3}/t + n_{HBO_2}/t + 3n_{(HBO_2)_3}/t, \tag{4}$$

where $n_{B_2O_3}/t$ equals the number of moles of $B_2O_{3(l)}$ lost from the boat per unit time, and $n_{H_3BO_3}/t$, n_{HBO_2}/t and $n_{(HBO_2)_3}$ are the number of moles of each gaseous boron species formed per unit time.

Dividing by the total number of moles of $H_2O_{(g)}$ and nitrogen flow gas which passed through the system in unit time (neglecting the small amount of gaseous boron species) and multiplying by the total pressure, P, of the system (equal to the external barometric pressure) one obtains:

$$2\left(\frac{n_{B_2O_3}/t}{n_{tot.}/t}\right)P = P_b = \left(\frac{n_{H_3BO_3}/t}{n_{tot.}/t}\right)P + \left(\frac{n_{HBO_2}/t}{n_{tot.}/t}\right)P + 3\left(\frac{n_{(HBO_2)_3}/t}{n_{tot.}/t}\right)P \tag{5}$$

or,

$$P_b = p_{H_3BO_3} + p_{HBO_2} + 3p_{(HBO_2)_3} \tag{6}$$

Combining (6) with (1'), (2') and (3'),

$$P_b = K^{1/2}_{p_1}\, p^{3/2}_{H_2O} + K^{1/2}_{p_2}\, p^{1/2}_{H_2O} + 3K^{1/2}_{p_3}\, p^{3/2}_{H_2O}. \tag{7}$$

When p_{HBO_2} is very small compared to $p_{H_3BO_3}$ and/or $p_{(HBO_2)_3}$,

$$P_b \approx (K^{1/2}_{p_1} + 3K^{1/2}_{p_3})\, p^{3/2}_{H_2O}, \text{ and} \tag{8}$$

$$\log P_b \approx 3/2 \log p_{H_2O} + \log (K^{1/2}_{p_1} + 3K^{1/2}_{p_3}). \tag{9}$$

Therefore, from equation (9), when p_{HBO_2} is small in comparison with the other gaseous species, a plot of $\log P_b$ vs. $\log p_{H_2O}$ will give a straight line with a slope of three-halves.

When p_{HBO_2} is large compared to both $p_{H_3BO_3}$ and $p_{(HBO_2)_3}$,

$$P_b \approx K^{1/2}_{p_2}\, p^{1/2}_{H_2O}, \text{ and} \tag{10}$$

$$\log P_b \approx 1/2 \log p_{H_2O} + \log K^{1/2}_{p_2} \tag{11}$$

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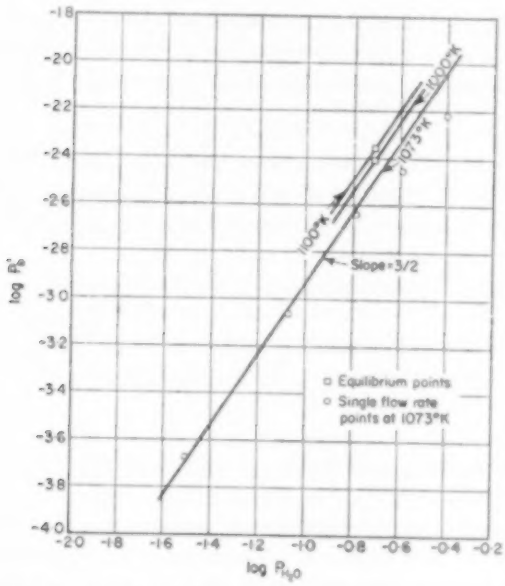

FIG. 1.—Pressure of gaseous boron species for various water pressures at 1000°, 1073° and 1100°K.

and, under these conditions, according to equation (11), a plot of log P_b vs. log p_{H_2O} will give a straight line with a slope of one-half.

At any point between these two pressures extremes, a log P_b vs. log p_{H_2O} plot will give a curved line varying in slope between three-halves and one-half. Thus, the line of

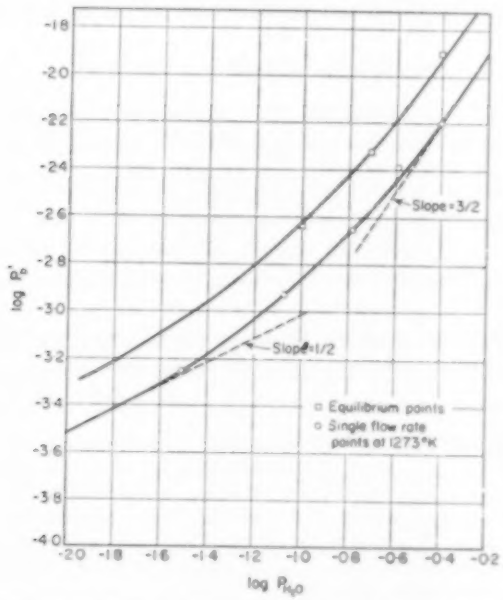

FIG. 2.—Pressures of gaseous boron species for various water pressures at 1273°K.

unit slope reported previously[3] indicates a mixture of gaseous species. A slope of 3/2 is found for the plot of data at 1073°K in Fig. 1, but at 1273°K and low water pressures a log P_b vs. log P_{H_2O} plot approaches slope one-half as shown in Fig. 2.

THE HEAT OF FORMATION OF $HBO_{2(g)}$

Appreciable concentrations of $HBO_{2(g)}$ were observed only at 1273°K in the water vapour region studied, i.e. where the slope of the equilibrium curve approaches one-half, and it was necessary to use a Third Law calculation to obtain the heat of formation of this gas.

Considering reaction (2) to be the only one of importance at 1273°K at a water vapour pressure of $1{\cdot}59 \times 10^{-2}$ atm, one finds at equilibrium: $P_b = P_{HBO_2} = 4{\cdot}76 \times 10^{-4}$ atm. From (2′) the equilibrium constant is found to be, $K_{P_2} = 1{\cdot}425 \times 10^{-5}$, and from this, $\Delta F/T_{1273} = +22{\cdot}17$ e.u. From this value of $\Delta F/T$ one calculates* $\Delta H_{f_{0°K}}[HBO_{2(g)}] = -135{\cdot}19$ kcal/mole.

A minor refinement of this heat value may be carried out by correcting for the small concentration of $H_3BO_{3(g)}$ and $(HBO_2)_{3(g)}$ present at this temperature and water vapour pressure. One finds: $P_{H_3BO_3(g)} = 0{\cdot}28 \times 10^{-4}$ atm. Also, from WHITE's[6] suggested values for the free energy function and heat of formation of $(HBO_2)_{3(g)}$ one obtains: $3P_{(HBO_2)_3(g)} = 0{\cdot}26 \times 10^{-4}$ atm. From this work, therefore, at 1273°K and a water vapour pressure of $1{\cdot}59 \times 10^{-2}$ atm, $P_{HBO_2(g)} = 4{\cdot}22 \times 10^{-4}$ atm. From this value, one obtains $\Delta H_{f_{0°K}}[HBO_{2(g)}] = -134{\cdot}88$ kcal/mole.

Consideration must be given to the uncertainties of the thermodynamic values used in this determination. The heats of formation of $H_2O_{(g)}$ and $B_2O_{3(c)}$ are quite accurately known, as is also the free energy function for $H_2O_{(g)}$. Data on HBO_2 are fairly reliable but there may be a rather large uncertainty in the free energy function for $B_2O_{3(l)}$.[11]

Applying these uncertainty values as limits, one finds that the heat of formation of $HBO_{2(g)}$ is:

$$\Delta H_{f_{0°K}}[HBO_{2(g)}] = -134{\cdot}9 \pm 1 \text{ kcal/mole.}$$

This value compares very favourably with that of WHITE[5,6] of $-135{\cdot}0 \pm 2{\cdot}5$ kcal/mole and with that of CHUPKA and BERKOWITZ[4] of $-134{\cdot}0 \pm 2{\cdot}5$ kcal/mole.

THE HEAT OF FORMATION OF $(HBO_2)_{3(g)}$

From the equilibrium data at a water vapour pressure of $3{\cdot}96 \times 10^{-1}$ atm, and after correcting for $H_3BO_{3(g)}$ and $HBO_{2(g)}$ present, the pressure of $(HBO_2)_{3(g)}$ was found to be $1{\cdot}78 \times 10^{-3}$ atm at 1000°K, $2{\cdot}48 \times 10^{-3}$ atm at 1100°K and $1{\cdot}91 \times 10^{-3}$ atm at 1273°K.

These pressure values are considerably more uncertain than the pressure obtained previously for the determination of the heat of formation of $HBO_{2(g)}$. In the case of

* In this and other calculations in this work, the following sources were used for free energy function and heat of formation values:

$(F^\circ - H_0^\circ/T)[HBO_{2(g)}]$;	WHITE *et al.*[6]
$(F^\circ - H_0^\circ/T)$ and $\Delta H_{f_{0°K}}[B_2O_{3(c,l)}]$;	EVANS *et al.*[9]
$(F^\circ - H_0^\circ/T)$ and $\Delta H_{f_{0°K}}[H_3BO_{3(g)}]$;	RANDALL, Unpublished work.
$(F^\circ - H_0^\circ/T)$ and $\Delta H_{f_{0°K}}[H_2O_{(g)}]$;	National Bureau of Standards.[10]

[9] W. EVANS, D. WAGMAN and E. PROSEN, National Bureau of Standards, Report No. 6252 (1958).
[10] *Selected Values of Thermodynamic Functions.* National Bureau of Standards, Series III. U.S. Government Printing Office, Washington, D.C. (1947).
[11] W. H. EVANS, National Bureau of Standards, Washington, D.C. Private communication (1960).

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TABLE 4

T(°K)	$P_{(HBO_2)_{3(g)}}$ (atm)	K_{p_3}	$\Delta H°_{f_{0°K}}$
1000	$1{\cdot}78 \times 10^{-3}$	$5{\cdot}02 \times 10^{-5}$	−536·3
1100	$2{\cdot}48 \times 10^{-3}$	$9{\cdot}76 \times 10^{-5}$	−537·7
1273	$1{\cdot}91 \times 10^{-3}$	$5{\cdot}79 \times 10^{-5}$	−538·5

$(HBO_2)_{3(g)}$, at the above three temperatures, the corrections for $HBO_{2(g)}$ and $H_3BO_{3(g)}$ present amount to approximately 50 per cent of the total measured P_t pressure. The determined pressures of $(HBO_2)_{3(g)}$ are therefore dependent to a large extent upon the reliability of the thermodynamic values used in calculating the pressures of $HBO_{2(g)}$ and $H_3BO_{3(g)}$ present.

Table 4 gives the results of Third Law calculations to obtain the heat of formation of $(HBO_2)_{3(g)}$. The most probable value for the heat of formation of the trimer is found to be −537·5 kcal/mole, at 0°K.

A Second Law calculation gives a heat of reaction for reaction (3) of +2·4 kcal in the temperature range 1000°–1273°K. From this, the heat of formation of $(HBO_2)_{3(g)}$ at 0°K is found to be −534·1 kcal/mole. The Second Law calculation, however, is more sensitive to small pressure errors, and the heat of formation obtained from the Third Law calculation is considered to be the more reliable figure.

It is difficult to assign an uncertainty value to this heat of formation since some of the thermodynamic functions used in its determination are estimated, but it is believed that the uncertainty is of the order of ±3 kcal/mole. This value of −537·5 ± 3 kcal/mole is in excellent agreement with that of −537 ± 10 kcal/mole suggested by WHITE[6], and −5·40 ± 10 suggested by CHUPKA and BERKOWITZ[4].

It is possible to draw some conclusions as to the magnitude of the heat of formation of $(HBO_2)_{3(g)}$ from the work of STACKELBERG *et al.*[1].

In studying the sublimation of $H_3BO_{3(c)}$ in a water vapour atmosphere according to,

$$H_3BO_{3(c)} = H_3BO_{3(g)} \tag{12}$$

these investigators observed at 109°C and under various water vapour pressures that the rate of sublimation of $H_3BO_{3(c)}$ was independent of the water vapour pressure between 760 mm and 99 mm pressure of $H_2O_{(g)}$ within the limits of their experimental error (about ±10 per cent). From this one can show for the reaction

$$3H_3BO_{3(c)} = (HBO_2)_{3(g)} + 3H_2O_{(g)} \tag{13}$$

that the heat of formation of $(HBO_2)_{3(g)}$ at 0°K must be less negative then −538 kcal/mole. If, for example, the pressure of $(HBO_2)_{3(g)}$ from reaction (13) was one-ninth that of the pressure of $H_3BO_{3(g)}$ from reaction (12) at 109°C and the relatively low water vapour pressure of 100 mm Hg, the heat of formation of $(HBO_2)_{3(g)}$ at 0°K would be −537 kcal/mole.

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ALKALI AND ALKALINE EARTH RHENOHYDRIDES*†

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(*Received* 22 *January* 1960; *in revised form* 5 *May* 1960)

Abstract—It is shown that the compounds previously described by us[1] as rhenides are actually complex rhenohydrides of the general formula $Me^{I}(Re^{III}H_4)\cdot 2\text{–}4H_2O$, at least if prepared by the reduction of perrhenates with potassium in aqueous ethylenediamine. This has been demonstrated by *quantitatively* determining the *hydrogen* evolution during thermal decomposition.

UPON the appearance of our preliminary publication on rhenides[1] we were informed by WILKINSON[2] of the Imperial College, London, that these compounds may possibly constitute water soluble complex rhenium hydrides and that this problem could be investigated by means of nuclear magnetic resonance spectroscopy.

Independently MILLER and GINSBERG[3] of Columbia University informed us of their investigation of the structure of the potassium rhenide prepared by the reduction of $KReO_4$ with K metal in aqueous ethylenediamine.[4] They found that the NMR spectrum of this compound indicated the presence of hydridic hydrogen bound to the transition metal. Based on additional analytical evidence they assigned the formula $K_6(Re_2H_{14})\cdot 6H_2O$ to the product isolated by them.

In our former investigation[1] hydrogen evolution was proven only qualitatively. The *quantitative studies* of the hydrogen evolution during thermal decomposition, indicate conclusively that this compound is a complex rhenohydride corresponding to the formula $K(ReH_4)\cdot 2\text{–}4H_2O$, while the analogous barium compound has the composition $Ba(ReH_4)_2\cdot 4\text{–}8H_2O$. Contrary to MILLER and GINSBERG, however, we find a K/Re ratio of 1 : 1 (vs. their 3 : 1) and a Re/H^- ratio of 1 : 4 (vs. their 1 : 7).

EXPERIMENTAL

Materials

Ammonium perrhenate c.p. was obtained from the University of Tennessee. Standard solutions were prepared by weighing out the dried material.

Potassium metal sticks "purified" were purchased from the Baker Chemical Company.

Anhydrous ethylenediamine was prepared by refluxing 98 per cent ethylenediamine (Eastman Kodak) over KOH pellets for several hours followed by a distillation in a nitrogen atmosphere.

Oxygen-free, anhydrous isopropanol was obtained by refluxing c.p. grade material (Baker Chem. Co.) with sodium isopropoxide, and subsequent distillation in a nitrogen atmosphere.

The very strong acidic sulphonic acid cation exchange resin AMBERLITE IR-120 was obtained

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[1] J. G. FLOSS and A. V. GROSSE, *J. Inorg. Nucl. Chem.* **9**, 318 (1959). See also A. V. GROSSE, *Z. Naturf.* **8b**, 533 (1953) and literature cited there.

[2] G. WILKINSON. Private communication (1959).

[3] A. P. GINSBERG. Private communication (1959); A. P. GINSBERG, Dissertation, Columbia University, New York (1959); A. P. GINSBERG, J. M. MILLER, J. R. CAVANAUGH and B. P. DALEY, *Nature, Lond.* In press.

[4] J. B. BRAVO, E. GRISWOLD and J. KLEINBERG, *J. Phys. Chem.* **58**, 18 (1954).

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from the Rohm & Haas Co. The hydrogen form of this resin was converted to the ammonium form by flushing the exchange column with 5 per cent ammonia solution.

Preparation of potassium and barium rhenohydride

One hundred millilitre anhydrous ethylenediamine was added to a 500 ml four-neck flask, equipped with a vibration mixer (manufactured by "Chemie Apparatebau" Zurich, Switzerland, for Fisher Scientific Co.), gas inlet tube, reflux condenser with a stock type mercury gas valve attached to it, and a thermometer, after the entire apparatus had been flushed with a slow stream of prepurified nitrogen for at least 30 min. A clean piece of potassium ($\simeq$1 g) was then added through the thermometer joint, and the solution heated to about 70°C by means of a "Glas-Col" heater. The potassium melted without reacting with the ethylenediamine. The heating was then discontinued and by operating the vibration mixer the molten potassium was smashed into tiny globules which dissolved in ethylenediamine with a deep blue colour, similar to that of potassium in liquid ammonia. The thermometer was then taken out temporarily and a few drops of warm aqueous NH_4ReO_4 solution were added through the thermometer joint by means of a pipette, and were immediately reduced by the potassium. More solution was added until the blue colour of the ethylenediamine solution was about to disappear. Then another piece of K-metal was added which melted and dissolved in the solution. The addition of an NH_4ReO_4-solution and K-metal alternately was continued for approximately 2 hr until all of the perrhenate solution had been consumed (10 ml solution, containing 0·70 g NH_4ReO_4, equivalent to 0·49 g Re). An excess of potassium in ethylenediamine was then destroyed by adding a few drops of water. During the entire operation a slow stream of prepurified nitrogen was passed through the system continuously.

The resulting suspension of potassium hydroxide, potassium rhenohydride and some unreduced perrhenate was allowed to cool to room temperature. The precipitate was then separated from the ethylenediamine by filtration through a fritted glass filter under reduced pressure, washed several times with anhydrous diethyl ether and finally dried *in vacuo*. This white or very slightly yellowish solid contained approximately 0·50–0·60 g potassium rhenohydride, 0·10–0·20 g $KReO_4$, negligible amounts of lower oxides of rhenium or metallic rhenium (below 1 per cent of total Re content) and large amounts of KOH.

This crude product was extracted several times with anhydrous i-propanol or ethanol in order to remove KOH and unreduced $KReO_4$ as described by KLEINBERG *et al.*[3,4] The residue containing all of the rhenohydride was thoroughly washed with anhydrous diethyl ether and dried *in vacuo*. It was then dissolved in a few ml of ice cold H_2O or 2N KOH solution. For further purification or conversion into barium rhenohydride, this solution was fed into an ion exchange column filled with the cation exchange resin AMBERLITE IR-120 in its ammonium form and 5 per cent ammonia solution as fluid phase, (flow rate: $\simeq$ 0·025 ml min^{-1} cm^{-3} bed volume). The effluent was checked continuously for rhenohydride and potassium ions by sampling a few drops and adding these to a TlOH-solution or a solution of $Bi(OH)_3$ in strong NaOH solution,[1] or subjecting them to a flame test. As soon as a rhenohydride break-through was observed the receptacle was changed and the ammonium rhenohydride collected. Exchange column and receptacle were kept at 0°C by means of external cooling. When the potassium break-through was observed or when the rhenohydride concentration in the effluent was finally found to become negligible, the operation was discontinued. The rhenohydride content of the solution was determined analytically and the stoicheiometric amount of a KOH or $Ba(OH)_2$ solution was added to an aliquot part of the effluent. Potassium or barium rhenohydride was obtained from this colourless clear solution by evaporation to dryness, *in vacuo*, preferably at 0°C, as a white microcrystalline solid (yield of potassium rhenohydride 0·60 g $\simeq$ 77 per cent). Larger crystals can be obtained by recrystallizing this compound very carefully from a saturated, cold, solution in a water ethanol mixture. (The solubility of potassium rhenohydride in water is of the same order of magnitude as that of KOH.)

All of these operations have to be conducted in a closed system under the protection of an inert atmosphere. Solutions which do not contain appreciable amounts of free hydroxide and ammonium rhenohydride solutions have to be kept at 0°C, lest the rhenohydrides decompose to rhenium metal, hydrogen and hydroxide.

Typical analyses for potassium and barium rhenohydride, including their hydrogen content, are given in the next section.

Both compounds, i.e. potassium and barium rhenohydride, contained no appreciable amounts of

perrhenates. This was demonstrated by adding tetraphenyl arsonium chloride to solutions of these compounds after the rhenohydride had been decomposed by adding dilute HCl; no precipitate of tetraphenyl arsonium perrhenate could be observed.

This was further substantiated by investigating samples of potassium rhenohydride with a petrographic microscope equipped with a universal stage.* The samples were mounted on a microscopic slide using Kel-F fluorocarbon lubricant as a medium. The indices of refraction of $KReH_4 \cdot 2H_2O$, as determined with immersion liquids, are

$$n_\varepsilon = 1{\cdot}664 \pm 0{\cdot}001 \qquad n_\omega = 1{\cdot}671 \pm 0{\cdot}001$$

and the birefringence $= 0{\cdot}007 \pm 0{\cdot}002$.

The crystal fragments exhibited an interference figure indicating a uniaxial negative character of the crystals. Because of the low birefringence, however, it is possible that they are biaxial with a very small optic angle. $KReO_4$, on the other hand, crystallizes in optically positive tetragonal bipyramids.[5] The indices of refraction are:

$$n_\varepsilon = 1{\cdot}685 \pm 0{\cdot}001 \qquad n_\omega = 1{\cdot}640 \pm 0{\cdot}001$$

and the birefringence $= 0{\cdot}045 \pm 0{\cdot}002$.

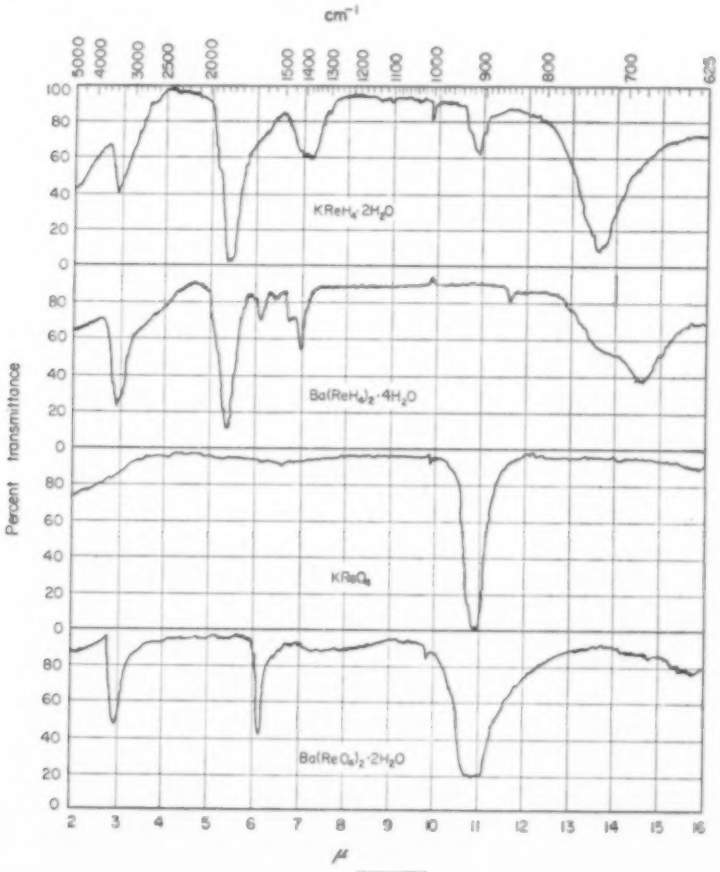

FIG. 1.

* These microscopic investigations were performed by Dr. E. H. WATSON, Bryn Mawr College, Bryn Mawr, Pa., subsequent to the Munich Congress.

[5] I. NODDACK and W. NODDACK, *Das Rhenium* p. 48, and literature cited there. Leopold Voss Verlag, Leipzig (1933).

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This extreme birefringence distinguishes $KReO_4$ from the rhenohydride immediately.

The infra-red spectra of potassium and barium rhenohydride provided another method for the detection of perrhenates in rhenohydrides (see page 40 and Figs. 1–5).

The oxidation equivalent of potassium and barium rhenohydride (n = meq. reducing power/mmole rhenium) on oxidation with permanganate in acidic solution[3,4] was found to be $n = 7{\cdot}9 \pm 0{\cdot}2$.

Thermal decomposition of rhenohydrides

The thermal decomposition of potassium and barium rhenohydrides was studied quantitatively. An all glass micro-apparatus was used, consisting of a tube (decomposition vessel), a U-tube, cooled in dry ice, for collecting water, a capillary mercury-manometer, and a bulb for collecting gases. The volume of this bulb was known precisely which permitted an accurate determination of the volume of the apparatus after the sample had been introduced. The entire apparatus was then evacuated and the sample in the decomposition tube was heated in an aluminium block, to about 450°C over a period of a couple of hours. At above 270°C a slow increase of the pressure could be observed which became more rapid with increasing temperature. After the hydrogen evolution had stopped, the heating was discontinued. When the apparatus had cooled to room temperature the increase in pressure was determined and the water was condensed in the U-tube at −78°C. The U-tube was then sealed off and the condensed water determined by weight.

The gas evolved proved to be hydrogen which was quantitatively determined by combusting an aliquot part of the content of the gas bulb in a CuO capillary attached to the decomposition apparatus. The total H_2 volume was calculated from the volume of the apparatus, the pressure, temperature and percentage of H_2 in the gas as determined by gas analysis. A correction was applied for the displacement of mercury in the manometer.

TABLE 1.—POTASSIUM RHENOHYDRIDE: $KReH_4{\cdot}2H_2O$
MOL. WT. = 265·47

Sample (mg)	H_2* (cm³ N.T.P.)	N/10HCl (ml)	Ph_4AsReO_4 (mg)	H_2O (mg)
25·3	$5{\cdot}3_9$ (corrected for impurities: 2·6% N_2; 97·4% H_2)	1·02	59·6	$1{\cdot}6_7$

i.e.

	Calculated		Found	
	Wt. %	Atoms (or moles)	Wt. %	Atoms (or moles)
K	14·72	1	15·8	1·1
Re	70·18	1	69·3	1 (standard)
H	1·52	4	1·89*	5·1 − 1·0 = 4·1
H_2O	13·58	2	6·6	1·96
O (as KOH)	—	—	7·14	
			100·7	

The empirical formula is therefore:

$$KReH_4{\cdot}2H_2O + 0{\cdot}1KOH$$

* i.e. H_2 collected during thermal decomposition of sample; 1 g at H per g at Re has to be subtracted from this value, since it is due to the formation of KOH from $KReH_4{\cdot}2H_2O$ (or BaO from $Ba(ReH_4)_2{\cdot}4H_2O$) during thermal decomposition.

After the thermal decomposition the solid residue was analysed for its total rhenium, and potassium or barium content.

Typical results of these experiments are listed in Table 1 below:

It should be noted that the above figures differ from previous ones;[1] this is due to the difference in water content, since the present compound contained $4H_2O$, whereas the previous sample contained $8H_2O$. The Ba : Re ratio is essentially the same. The water content varies and depends upon drying conditions in a desiccator.

Infra-red spectra

The infra-red spectra of potassium and barium rhenohydride as well as potassium and barium perrhenate were recorded with a Perkin–Elmer Infra-red Spectrophotometer, Model 21. They are shown in Figs. 1–5. The samples were mixed and pressed with KBr in an inert atmosphere (concentration of samples in KBr 0·5 per cent, thickness 0·5 mm).

The presence of perrhenates in rhenohydrides in concentrations above 1 per cent can be readily determined quantitatively by using the perrhenate absorption peak at 915 cm^{-1}.

Analytical methods

The analytical procedures which were used for the determination of potassium and barium, total rhenium and the oxidation equivalent have already been described.[1]

TABLE 2.—BARIUM RHENOHYDRIDE: $Ba(ReH_4)_2 \cdot 4H_2O$
MOL. WT. = 590·11

Sample (mg)	H_2* (cm^3 N.T.P.)	$BaSO_4$ (mg)	Ph_4AsReO_4 (mg)	H_2O (mg)
36·11	6·5$_6$ (corrected for impurities 6·5% N_2; 93·5% H_2)	16·9	74·7	1·8$_8$

i.e.

	Calculated		Found	
	Wt. %	Atoms (or moles)	Wt. %	Atoms (or moles)
Ba	23·28	1	27·5	1·19
Re	63·14	2	62·5	2·0 (standard)
H	1·37	8	1·62*	9·68 − 2·00 = 7·68
H_2O	12·21	4	5·15	3·70
O (as BaO)	—	—	5·36	
			102·2	

The empirical formula is therefore:

$$Ba(ReH_4)_2 \cdot 4H_2O + 0{\cdot}2Ba(OH)_2 \cdot 8H_2O$$

* i.e. H_2 collected during thermal decomposition of sample; 1 g at H per g at Re has to be subtracted from this value, since it is due to the formation of KOH from $KReH_4 \cdot 2H_2O$ (or BaO from $Ba(ReH_4)_2 \cdot 4H_2O$) during the thermal decomposition.

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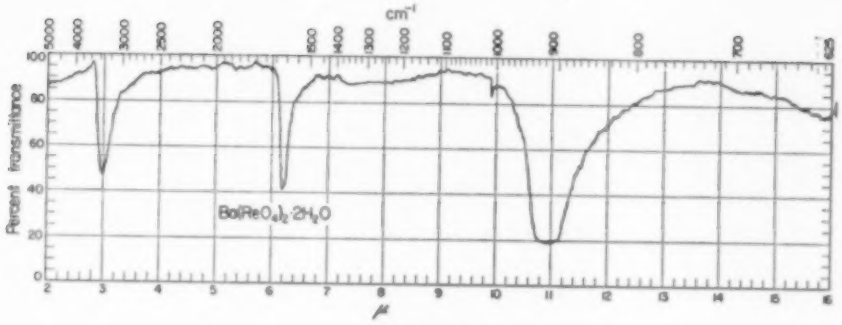

FIG. 2.

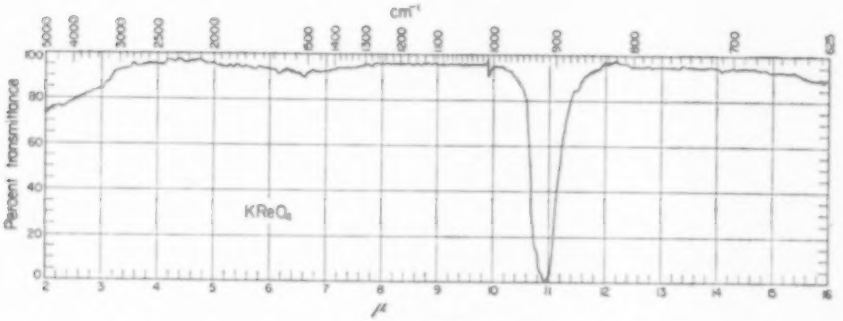

FIG. 3.

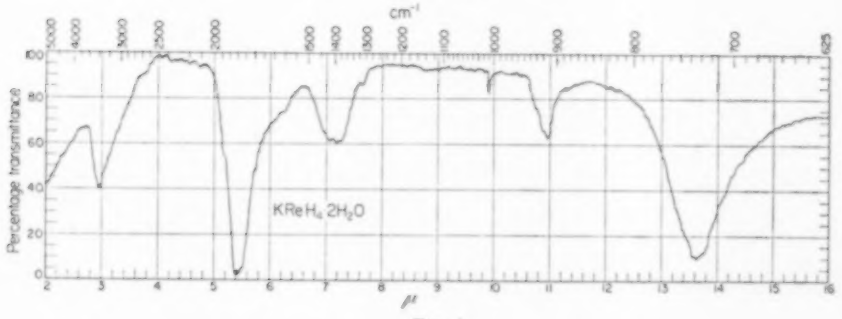

FIG. 4.

In addition to these methods the total rhenium content of the reaction products was also determined as tetraphenyl arsonium perrhenate.[6,7,8] An aliquot amount of rhenohydride solution was oxidized with hydrogen peroxide in an alkaline medium. Excess peroxide was destroyed by boiling. The solution was then neutralized ($6 < pH < 7$) with dilute hydrochloric acid and a concentrated solution of tetraphenyl-arsonium chloride added. The solution was then slowly cooled to 0°C and after several hours the crystalline tetraphenyl arsonium perrhenate was filtered, washed several times with cold, saturated tetraphenyl arsonium perrhenate solution and dried at 125°C.

[6] W. WILLARD and G. SMITH, *Industr. Engng. Chem. (Anal.)* **11**, 305 (1939).
[7] W. SMITH and S. LONG, *J. Amer. Chem. Soc.* **70**, 354 (1948).
[8] C. T. SIMS, E. W. WYLER, G. B. GAINES and D. M. ROSENBAUM, *A Survey of the Literature on Rhenium*, WADC Technical Report 56-319. ASTIA Document No. AD110596, p. 94 ff, and literature cited there.

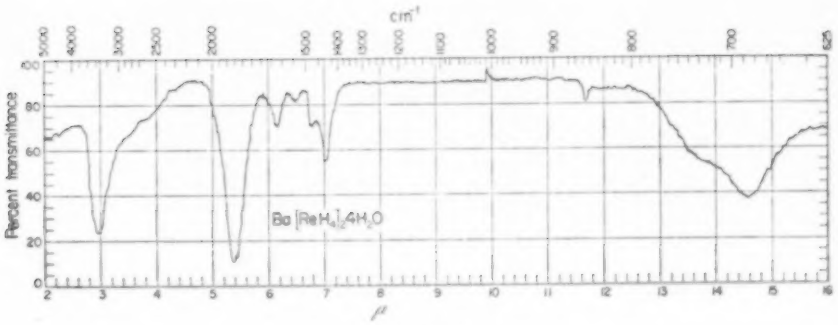

FIG. 5.

In order to determine ReO_4^- and ReH_4^- separately, in a solution *containing both ions*, the solution was acidified with HCl, whereupon the rhenohydride decomposed according to the equation

$$2(ReH_4)^- + 2\,H^+ \rightarrow 2Re + 5H_2$$

whereas *the perrhenate remained unaffected.* The rhenium metal was filtered and determined either as such or as tetraphenyl arsonium perrhenate after oxidation to perrhenate. The perrhenate was determined as described above.

DISCUSSION

These experimental results demonstrate that the reduction of an aqueous perrhenate solution with a blue solution of K metal in anhydrous ethylenediamine yields the potassium salt of a complex rhenium hydride from which corresponding salts with different cations, e.g. Ba^{2+}, can be prepared by means of cation exchange methods.

Thermal decompositions of these compounds yield Re metal and 2·5 moles H_4 per gramme atom Re.

Complete analytical investigations of this reaction indicate that the ratio of Re/K and Re/Ba equals one and two respectively. The empirical formulae of potassium and barium rhenohydride are therefore $KReH_4 \cdot xH_2O$ and $Ba(ReH_4)_2 \cdot 2xH_2O$; x varies between two and four depending upon drying conditions. Thus their thermal decompositions follow the equations:

$$K(ReH_4) \cdot 2H_2O \rightarrow Re + 5/2\,H_2 + KOH + H_2O$$
$$Ra(ReH_4)_2 \cdot 4H_2O \rightarrow 2\,Re + 5\,H_2 + BaO + 3H_2O$$

These formulae are also consistent with the oxidation equivalent $n = 8$ in acidic media according to:

$$ReH_4^- + 4H_2O \rightarrow ReO_4^- + 2H_2 + 8H^+ + 8\,e$$

Considering the chemical properties of rhenium the existence of more than one defined complex rhenium hydride, with different valence states and co-ordination numbers of rhenium, is possible. This might account for the difference between our findings and those of MILLER and GINSBERG[3].

The hydrogen content of our original[1] lithium "rhenide" has not been determined; it is likely, however, that it will also prove to be a rhenohydride.

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The existence of a fairly stable complex rhenium hydride is the first example of a *transition metal* ion forming a complex hydride anion, which is not stabilized by co-ordination with strong complexing ligands, like carbonyl or cyclopentadienyl (for example, in such compounds as $[HFe(CO)_4]^-$, $[(C_5H_5)_2ReH_2]^+$, etc. This raises the question whether analogous hydrides of other transition metals can be prepared. Exploratory experiments in this direction are now being carried out.[9]

[9] J. G. Floss and A. V. Grosse, *J. Inorg. Nucl. Chem.* **16**, 44 (1960).

J. Inorg. Nucl. Chem., 1960, Vol. 16, pp. 44 to 47. Pergamon Press Ltd. Printed in Northern Ireland

TECHNETIUM ANALOGUES OF RHENOHYDRIDES*

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Abstract—It is shown that the Tc analogue of potassium rhenohydride, $K[ReH_4]\cdot 2H_2O$, can be obtained by reducing Tc-labelled NH_4ReO_4 solution with K in ethylenediamine. The distribution of Tc among the reaction products has been studied. Up to 90% of the Tc can be converted into a water soluble potassium technohydride.

It was discovered recently that the reduction of aqueous perrhenate solution with potassium metal in anhydrous ethylenediamine yields a complex potassium rhenohydride,[1,2] $K^+[Re^{III}H_4]^-\cdot 2\text{–}4\ H_2O$, and not potassium rhenide,[3–6] as has been assumed until now.

The reduction of NH_4ReO_4, labelled with $NH_4{}^{99}TcO_4$, with potassium in ethylenediamine and the subsequent investigation of the Tc-activity distribution in the products of this reaction, show that Tc analogues of the rhenohydrides, i.e., complex technohydrides, are obtained. Their stability, however, is less than that of the rhenohydrides.

EXPERIMENTAL

Materials. ^{99}Tc (20 μc/mg Tc; half-life: $2{\cdot}12 \times 10^5$ years) was obtained, as NH_4TcO_4, in dilute NH_4OH solution (0·5 mg Tc/ml soln) from the Oak Ridge National Laboratory. Of this solution 0·500 ml was diluted with H_2O and 1·4399 g of NH_4ReO_4 (obtained from the University of Tennessee), added. After the perrhenate had dissolved, the solution was brought to a total volume of 100·00 ml (solution I, containing 1·4399 g NH_4ReO_4 = 1·000 g Re, and 0·457 mg NH_4TcO_4 = 0·25 mg Tc). Ten millilitres of solution I were heated and further 0·8012 g NH_4ReO_4 (= 556·0 mg Re), was dissolved, obtaining solution II (containing 656·0 mg Re and 0·025 mg Tc; atomic ratio of Tc:Re ~ 1:14000). Solution II was used as such for the reduction experiments.

Analytical procedures. In order to determine the Tc-content of the Tc-labelled Re-compounds, samples were painted on aluminium planchets 1 in. in diameter and their relative activity was determined with an LS2 model GM counter (Technical Associates, Glendale, California), connected to a model LS-1000-A decade scaler (Eltronics, Inc., Philadelphia, Pennsylvania).

Tc-labelled perrhenates were determined either as $KReO_4$ or as $(C_6H_5)_4AsReO_4$. Tc-labelled rhenohydrides were decomposed with dilute HCl and the resulting Tc-labelled Re-metal was counted for its activity.

The activity determinations were carried out under identical geometric conditions and in the same counter. Corrections for β-ray self-absorption were made for varying thicknesses of the samples.

Reduction of Tc-*labelled* NH_4ReO_4. Ten millilitres of solution II were reduced with a blue solution of K in ethylenediamine, as described previously.[1] The raw reaction product was first extracted repeatedly with isopropanol or ethanol,[1,2,3] in order to remove the KOH and unreduced

* This research was supported by the U.S. Atomic Energy Commission, Contract AT(30-1)-2082, see U.S.A.E.C. Report No. NYO-2156. The Research Institute of Temple University, September 28, 1959.

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[2] A. P. Ginsberg, Ph.D. Dissertation, Columbia University, New York (1959); A. P. Ginsberg, J. M. Miller, J. R. Cavanaugh and B. P. Daley, *Nature, Lond.* In press.
[3] J. B. Bravo, E. Griswold and J. Kleinberg, *J. Phys. Chem.* **58**, 18 (1954).
[4] A. V. Grosse, *Z. Naturf.* **8b**, 533 (1953).
[5] J. G. Floss and A. V. Grosse, *J. Inorg. Nucl. Chem.* **9**, 318 (1959), and literature cited there.
[6] G. E. F. Lundell and H. B. Knowles, *J. Res. Nat. Bur. Stand.* **18**, 629 (1937).

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$KReO_4$ (and $KTcO_4$), then washed with anhydrous ether, thoroughly dried, and finally dissolved in approximately 10 ml of ice-water. During this last operation the rhenohydride decomposed partially, forming black Re-metal. The solution containing the $KReH_4$, was filtered, after a short time, from the Re-metal and small amounts of $KReO_4$ and the residue washed with small amounts of ice-water which was added to the $KReH_4$-filtrate. The $KReO_4$ was completely extracted from the residue with hot water. This $KReO_4$ solution was evaporated and the crystallized perrhenate weighed and its activity counted (6·0 mg Re, total relative activity 4100 counts/min). The Re metal residue was washed, dried and weighed and its activity determined (28 mg Re, total relative activity 54,000 counts/min). The filtrate containing the rhenohydride and some KOH was brought to a definite volume. To an aliquot part of this solution 4 N HCl was added in order to precipitate the Re of the $KReH_4$ as Re metal, which was filtered and weighed and its activity determined. The rest of the solution was evaporated to dryness yielding Tc-labelled $KReH_4 \cdot 2H_2O$ which was used for subsequent experiments.

A number of such reductions were carried out. The results of a typical experiment are given in Table 1, which shows, schematically, the Tc-activity distribution among the various Re-compounds isolated.

In order to interpret the results listed in Table 1, and to determine whether the Tc-activity in the $KReH_4 \cdot 2H_2O$, is due to admixed $KTcO_4$, or to a hypothetical $KTcH_4 \cdot xH_2O$, the following experiments were carried out:

(1) *Cocrystallization of pertechnetate with perrhenate.* An aqueous solution of 88·2 mg $KTcO_4$-labelled $KReO_4$ (total Tc-activity 500 counts/min), was partially evaporated at room temperature under reduced pressure. The $KReO_4$ crystals were filtered, washed with small amounts of ice-water, dried and weighed and their Tc-activity counted (55·2 mg $KReO_4$, total activity 175 counts/min). The $KReO_4$ and $KTcO_4$ which remained in solution were recovered by evaporating the filtrate to dryness (33.0 mg $KReO_4$, total activity 310 counts/min). This shows that part of the $KTcO_4$ crystallizes with the $KReO_4$, most likely by means of isomorphous replacement; the homogeneous distribution coefficient,[7] D, for this process has the *approximate* value:

$$D = \frac{[KTcO_4]_{cryst} \cdot [KReO_4]_{soln}}{[KTcO_4]_{soln} \cdot [KReO_4]_{cryst}} = 0{\cdot}3$$

(2) *Coprecipitation of* Tc *with* $(C_6H_5)_4As\,ReO_4$. When Tc-labelled $KReO_4$ is completely precipitated as tetraphenyl arsonium perrhenate, the *entire* Tc-*activity* is found in this precipitate.

(3) *Fractional crystallization of* $KReO_4$ *from an alkaline solution of inactive* $KReH_4$ *and* Tc-*labelled* $KReO_4$. Ten millilitres of a 2 N KOH solution of inactive $KReH_4$ (46·2 mg), and Tc-labelled $KReO_4$, were evaporated at room temperature under reduced pressure to a volume of approximately 1 ml. The $KReO_4$ crystals were isolated; they contained about 90 per cent of the total Tc-activity. Ten per cent of the Tc-activity was found in the remaining solution together with very small amounts of $KReO_4$ (less than 1 mg), and all of the $KReH_4$. This indicates that in an alkaline medium the $KTcO_4$ is *not reduced* by the $KReH_4$ and can be recovered as such, i.e. in the $KReO_4$ crystals.

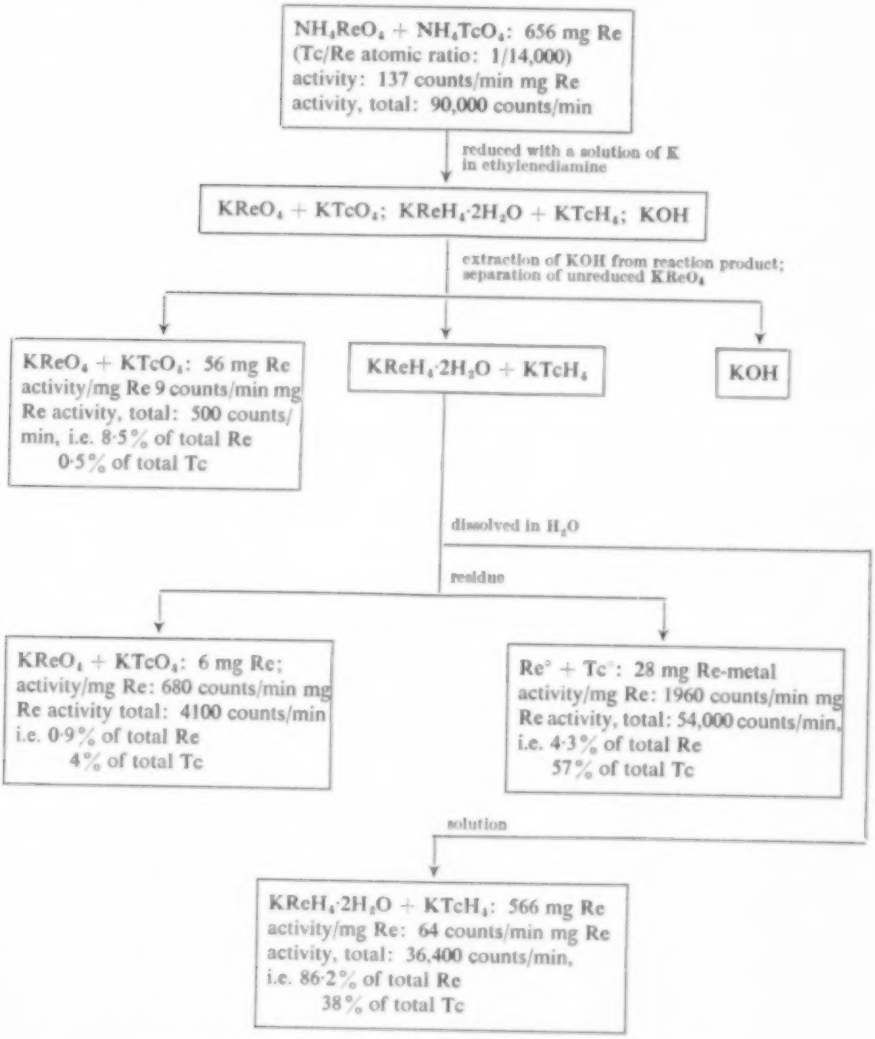
(4) *Fractional crystallization of* $KReO_4$ *from an alkaline solution of inactive* $KReO_4$ *and* Tc-*labelled* $KReH_4$. Ten millilitres of 2 N KOH solution, saturated in $KReO_4$, and containing 52·3 mg of Tc-labelled $KReH_4$ (isolated from the products of the reduction of Tc-labelled NH_4ReO_4 with K in ethelynediamine) were evaporated at room temperature under reduced pressure to about 1 ml. The $KReO_4$ crystalls were isolated; they showed negligible amounts of Tc-activity. The *entire* Tc-*activity remained in solution* with the rhenohydride; this was determined by acidifying the solution and determining the Tc-activity of an aliquot part of the Re-metal, obtained according to the equation:

$$[ReH_4]^- + H^+ \rightarrow Re^\circ + 5/2\,H_2$$

(5) *Reduction of* TcO_4^- *with* $[ReH_4]^-$ *in acidic solution.* Fifteen millilitres of a 2 N KOH solution containing 46·0 mg inactive $KReH_4$ and 5 mg Tc-labelled $KReO_4$ were acidified with a 6 N HCl at $\simeq$25°C. The metallic rhenium obtained from the resulting decomposition of the rhenohydride was isolated, washed very carefully with hot water, dried *in vacuo*, weighed and its activity determined.

[7] A. C. Wahl and N. A. Bonner, *Radioactivity Applied to Chemistry* p. 106 ff. John Wiley, New York (1951).

TABLE 1.—ACTIVITY DISTRIBUTION IN THE PRODUCTS OF THE REDUCTION OF NH_4ReO_4 LABELLED WITH $NH_4{}^{99}TcO_4$ WITH K-METAL IN AQUEOUS ETHYLENEDIAMINE


NH4ReO4 + NH4TcO4: 656 mg Re
(Tc/Re atomic ratio: 1/14,000)
activity: 137 counts/min mg Re
activity, total: 90,000 counts/min
reduced with a solution of K in ethylenediamine
KReO4 + KTcO4; KReH4·2H2O + KTcH4; KOH
extraction of KOH from reaction product; separation of unreduced KReO4
KReO4 + KTcO4: 56 mg Re
activity/mg Re 9 counts/min mg Re activity, total: 500 counts/min, i.e. 8·5% of total Re
0·5% of total Tc
KReH4·2H2O + KTcH4
KOH
dissolved in H2O
residue
KReO4 + KTcO4: 6 mg Re;
activity/mg Re: 680 counts/min mg Re activity total: 4100 counts/min
i.e. 0·9% of total Re
4% of total Tc
Re° + Tc°: 28 mg Re-metal
activity/mg Re: 1960 counts/min mg Re activity, total: 54,000 counts/min,
i.e. 4·3% of total Re
57% of total Tc
solution
KReH4·2H2O + KTcH4: 566 mg Re
activity/mg Re: 64 counts/min mg Re
activity, total: 36,400 counts/min,
i.e. 86·2% of total Re
38% of total Tc

It exhibited the *entire* Tc-*activity* originally present as $KTcO_4$. The perrhenate remaining in solution was isolated as Ph_4AsReO_4, and *proved to be inactive*. This experiment shows that pertechnetate is reduced by rhenohydride in acidic solution to an insoluble species of Tc, presumably Tc-metal.

In the light of these findings *another reduction* of NH_4ReO_4 labelled with NH_4TcO_4 (equiv. 628 mg Re and 0·05 mg Tc, atomic ratio Tc:Re $\simeq$ 1:7000) with K in ethylenediamine was performed. In order to keep the partial decomposition of the rhenohydride to Re-metal at a minimum, the raw product was dissolved in cold (0°C) 2 N KOH after the extraction with isopropanol.[2] The rhenohydride was recovered from this KOH solution as a white microcrystalline solid, by adding oxygen-free methanol and pipetting this solution under the surface of a large excess of isopropanol. Under these conditions only minute amounts of Re-metal were obtained (3·8 mg = 0·6 per cent) which

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exhibited 3·4 per cent of the total Tc-activity. The rhenohydride (equiv. 545·2 mg Re = 86·7 per cent of total Re), on the other hand, *contained* 90 *per cent of the total* Tc-*activity*. The concentration of technohydride in rhenohydride was ≃0·015 mole per cent. The $KReO_4$, separated from the reaction mixture during the alcohol extraction (equiv. 78·3 mg Re = 12·5 per cent of total Re) contained 7·2 per cent of the total Tc-activity.

DISCUSSION

The reduction of an aqueous solution of NH_4ReO_4 labelled with NH_4TcO_4 with a blue solution of potassium in anhydrous ethylenediamine and the quantitative separation of the products of this reaction yields $KReH_4 \cdot 2H_2O$, which contain up to 90 per cent of the total initial Tc. This Tc-content cannot be due to admixed $KTcO_4$, because when a $KReO_4$ solution is added to an alkaline solution of Tc-labelled $KReH_4$ and the $KReO_4$ is then separated again from the rhenohydride, either by fractional crystallization or by evaporating the solution to dryness and treatment of the residue with isopropanol,[3] the Tc-activity stays with the rhenohydride and the perrhenate is shown to be inactive. If, on the other hand, a $KReO_4$ solution, containing $KTcO_4$, is added to an *alkaline* solution of Tc-free $KReH_4$, the Tc-activity remains with the perrhenate during the separation of the perrhenate from the rhenohydride.

It must be concluded therefore that the described reduction of NH_4TcO_4, using perrhenate as a carrier, yields a compound of a lower oxidation number of Tc, which is soluble in aqueous hydroxide solutions. This is most likely a complex potassium technohydride, $K^+[TcH_4]^- \cdot xH_2O$, in view of its similar chemical behaviour to $K^+[ReH_4]^- xH_2O$ and the fact that most Tc-compounds are isomorphous with the corresponding Re-compounds.

The Re metal, produced by the partial decomposition of the rhenohydride, while dissolving the raw product in ice-water after the alcohol extraction, exhibits a very high Tc-activity (57 per cent of total Tc-activity vs. 4·3 per cent of total Re i.e. a Tc:Re atomic ratio of ≃1:4000. If the rhenohydride is dissolved in cold 2 N KOH instead of water the degree of this decomposition is considerably less (0·6 per cent of total Re, 3·4 per cent of total Tc). This indicates that the technohydrides are even more sensitive to protons and consequently less stable than the corresponding rhenohydrides. The above interpretation is supported further by polarographic studies of $KTcO_4$ in 2 M KCl, where an eight-electron reduction was observed,[8] which is analogous to the polarographic reduction of $KReO_4$ solutions.[8,9]

COBBLE[10] attempted, unsuccessfully, the preparation of technetides, i.e. the technetium analogues of rhenides, by reducing an aqueous pertechnetate solution in a Jones reductor, presumably in acidic medium. Under those conditions no technohydrides can be obtained, since they are unstable in acidic media and decompose immediately, if formed at all.

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[9] J. J. LINGANE, *J. Amer. Chem. Soc.* **64**, 1001 (1942).
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J. Inorg. Nucl. Chem., 1960, Vol. 16, pp. 48 to 51. Pergamon Press Ltd. Printed in Northern Ireland

THE THERMAL STABILITY OF METAL AMMINES—III

PLATINUM(II) AMMINES[1]

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Abstract—The generally accepted temperature of 250°C for the conversion of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ to *trans*-$[Pt(NH_3)_2Cl_2]$ leads to extensive decomposition to elemental Pt in a relatively short time. Although standard thermogravimetric analyses indicate that *trans*-$[Pt(NH_3)_2Cl_2]$ is stable to 270°C, constant-temperature treatment in furnaces indicates a much lower practical decomposition temperature. At 200°C the thermal decomposition is slow enough that it is possible to effect an essentially quantitative conversion of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ to *trans*-$[Pt(NH_3)_2Cl_2]$.

IN attempting to prepare *trans*-$[Pt(NH_3)_2Cl_2]$ by the thermal decomposition of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$[2] we encountered difficulties which prompted us to investigate this reaction more carefully. It is repeatedly stated in the literature that heating $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ at 250°C until ammonia evolution ceases converts it to *trans*-$[Pt(NH_3)_2Cl_2]$.[2] These statements all appear to stem from REISET's original observations,[3] and there seems to have been no note made of the report by GRINBERG and PTITSYN[4] that the decomposition temperature of *trans*-$[Pt(NH_3)_2Cl_2]$ is 227°C in a stream of dry air and of the report by NIKOLAEV and RUBINSHTEĬN[5] that differential thermal analysis indicates a decomposition temperature of 230°C for $[Pt(NH_3)_2Cl_2]$.

Our initial experiments showed 250°C to be too high a temperature for clean conversion of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ to *trans*-$[Pt(NH_3)_2Cl_2]$. In all cases there was obvious darkening of the sample within an hour and greater loss of weight than expected for conversion to the yellow diammine. We have, therefore, reinvestigated the thermal decomposition of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ both by thermogravimetric analysis and by heating at constant temperature in static and flow systems.

Fig. 1 shows conventional TGA traces for both $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ and *trans*-$[Pt(NH_3)_2Cl_2]$, whereas Fig. 2 shows a modified TGA run for *trans*-$[Pt(NH_3)_2Cl_2]$ in which the temperature was taken to 250°C as usual and then held constant. In all cases the final residue was identified as metallic platinum by X-ray diffraction. The two conventional curves indicate that the diammine started to decompose about 270°C and then went rapidly to metallic Pt. For $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ the weight loss to the first plateau corresponded closely to that calculated for the loss of one molecule of

[1] Part II: L. R. OCONE, J. R. SOULEN and B. P. BLOCK, *J. Inorg Nucl. Chem.* **15**, 76 (1960).
[2a] G. BRAUER, *Handbuch der Präparativen Anorganischen Chemie* p. 1181. Ferdinand Enke Verlag, Stuttgart (1954); [b] J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* Vol. 16, p. 261. Longmans, Green, London (1937); [c] R. N. KELLER, *Inorg. Synth.* **2**, 250 (1946).
[3] J. REISET, *C.R. Acad. Sci., Paris* **18**, 1103 (1844).
[4] A. A. GRINBERG and B. V. PTITSYN, *Izv. Sektora Platiny i Drug. Blagorod. Metal. Inst. Obschei i Neorg. Khim., Akad. Nauk SSSR* **9**, 73 (1932).
[5] A. V. NIKOLAEV and A. M. RUBINSHTEĬN, *Izv. Sektora Platiny i Drug. Blagorod. Metal. Inst. Obschei i Neorg. Khim., Akad. Nauk SSSR* **21**, 126 (1948).

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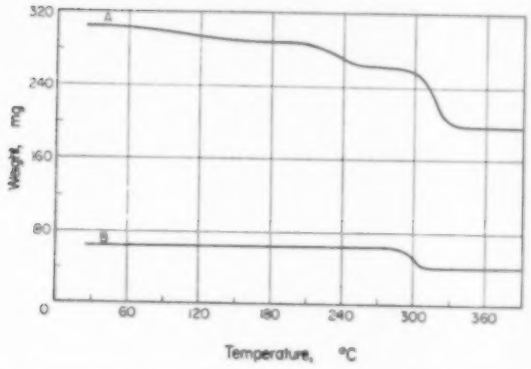

FIG. 1.—Thermogravimetric curves. Curve A: $[Pt(NH_3)_4]Cl_2 \cdot H_2O$, Curve B: *trans*-$[Pt(NH_3)_2Cl_2]$.

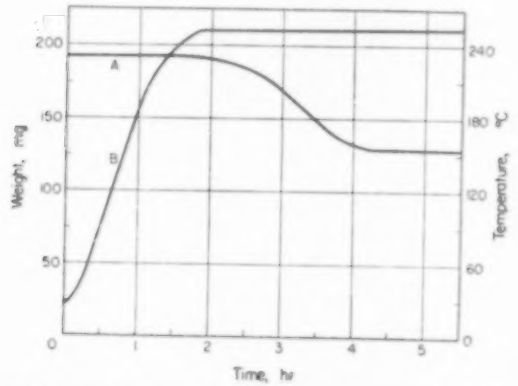

FIG. 2.—Modified thermogravimetric study of *trans*-$[Pt(NH_3)_2Cl_2]$. Curve A: weight of sample, Curve B: temperature.

water and two of ammonia. The weight loss to the second plateau corresponded to the loss of the remaining ammonia and the chlorides. For $[Pt(NH_3)_2Cl_2]$ the weight loss to the plateau corresponded to the formation of elemental platinum.

Although the curves in Fig. 1 indicate that $[Pt(NH_3)_2Cl_2]$ is stable at 250°C, Fig. 2 clearly shows that it is not. A careful examination of the original tracing shows initiation at about 220°C of a very slight loss in weight, which continues as the temperature is raised to and held at 250°C until the diammine is completely converted to platinum. In about 4·5 hr starting from room temperature a 192·5 mg sample was completely decomposed to platinum. After the initial induction period there is a constant rate of weight loss for a period corresponding to decomposition of over half the material, which suggests that this decomposition may be zero order. Although it does not appear autocatalytic, a careful study of the decomposition products would be required to decide because there may well be two processes involved, i.e. loss of NH_3 and loss of Cl_2. A zero order process is, however, reasonable and was found in a similar study of chromium(III) ammines.[6]

[6] N. D. PESCHKO and B. P. BLOCK, *J. Inorg. Nucl. Chem.* **15**, 71 (1960).

Table 1.—Results of heating platinum(II) ammines in a furnace

Substance	Atmosphere	Temp. (°C)	Time (hr)	Wt. loss (%)
$[Pt(NH_3)_4]Cl_2 \cdot H_2O$	air	250	1	16·5*
	air	234	17	43·*
	air	203	17	16·4*
	air	195	16	14·3
$[Pt(NH_3)_4]Cl_2$	air	250	2	38·5*
	air	200	6	10·6
	air	170	6	6·9
$[Pt(NH_3)_2Cl_2]$	air	250	2	31·7*
	N_2†	250	2	34·5*
	N_2‡	250	2	32·4*

* Pt visibly present
† static system
‡ flow system

Calculated weight losses: $[Pt(NH_3)_4]Cl_2 \cdot H_2O \rightarrow [Pt(NH_3)_2Cl_2]$ 14·78%, $[Pt(NH_3)_4]Cl_2 \cdot H_2O \rightarrow Pt$ 44·58%; $[Pt(NH_3)_4]Cl_2 \rightarrow [Pt(NH_3)_2Cl_2]$ 10·19%, $[Pt(NH_3)_4]Cl_2 \rightarrow Pt$ 41·59%; $[Pt(NH_3)_2Cl_2] \rightarrow Pt$ 34·97%.

The temperatures reported by the Russian investigators[4,5] for the decomposition points of *trans*-$[Pt(NH_3)_2Cl_2]$ thus correspond to the temperature at which loss in weight is first detectable in the thermogravimetric analysis of $[Pt(NH_3)_2Cl_2]$ under our conditions. We also confirm by thermogravimetric analysis the observation of Nikolaev and Rubinshteĭn[5] that water is not removed from $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ in a sharply defined step. The reason for this was not fully investigated, but it appears to be a rate phenomenon. Heating at 110°C leads to removal of all the water, and this is apparently also true for heating at 90–95°C.

Experiments at constant temperature, both in air and in nitrogen, fully confirm the instability of *trans*-$[Pt(NH_3)_2Cl_2]$ at 250°C. The results of several different runs are summarized in Table 1. It will be seen that, whether $[Pt(NH_3)_4]Cl_2 \cdot H_2O$, $[Pt(NH_3)_4]Cl_2$, or *trans*-$[Pt(NH_3)_2Cl_2]$ is heated at 250°C, there is extensive decomposition to elemental platinum within a relatively short time. On the other hand if $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ or $[Pt(NH_3)_4]Cl_2$ is heated at about 200°C, the residue after constant weight is reached corresponds closely to theoretical conversion to *trans*-$[Pt(NH_3)_2Cl_2]$. We have found it possible to prepare *trans*-$[Pt(NH_3)_2Cl_2]$ from $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ or $[Pt(NH_3)_4]Cl_2$ by heating at 195–200°C and following the weight loss closely, but the temperature is very critical and small increases in temperature seem to lead to decomposition if not corrected. Decomposition is quite readily detected visually by the darkening of the yellow *trans*-$[Pt(NH_3)_2Cl_2]$ as elemental platinum is formed.

The furnace experiments are not in exact agreement with the Russian work or with the thermogravimetric studies. We believe this to be due to the rapid rate of heating employed for thermogravimetry (300°C/hr), which undoubtedly causes a lag between the attainment of a given temperature and the observation of phenomena such as weight loss attributable thereto.

EXPERIMENTAL

$[Pt(NH_3)_4]Cl_2 \cdot H_2O$ was prepared by the method of Keller[3c]. It was converted to $[Pt(NH_3)_4]Cl_2$ by heating to constant weight at 110°C. 2·550 g of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ yielding 2·420 g of $[Pt(NH_3)_4]Cl_2$, exactly the calculated weight, in a typical run. The samples of *trans*-$[Pt(NH_3)_2Cl_2]$ were prepared by careful decomposition of hydrated or anhydrous $[Pt(NH_3)_4]Cl_2$ at about 200°C in a

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furnace. (Found: Pt 64·6, 64·2; NH_3 11·3, 11·4; Cl 22·1, 22·3. Calc. for $Pt(NH_3)_2Cl_2$; Pt 65·0, NH_3 11·3, Cl 23·6%).

The thermogravimetric curves were determined on a Chevenard Thermobalance as described earlier.[1] The furnaces used in the constant-temperature studies were a Type 62 1440W muffle furnace and a Type 70 750W tube furnace (Hevi Duty Electric Co.). Temperatures were regulated with an Ampliitrol regulator (Barber-Colman Co.) and measured with iron-constantan or chromel-alumel thermocouples.

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CHEMISTRY OF PHOSPHORUS FLUORIDES

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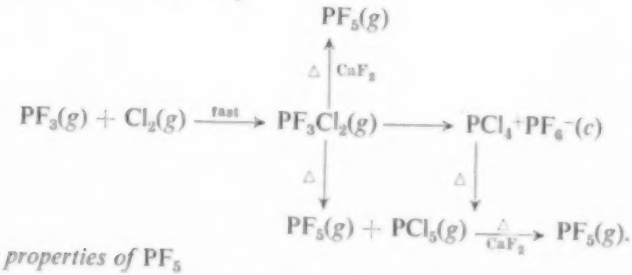
Abstract—Phosphorus tri- and pentafluorides were prepared in high yield and conversion by reaction of the respective chlorides and CaF_2 at 300–400°. The pentafluoride is a very strong acceptor molecule and forms complexes with amines, ethers, nitriles, sulphoxides and other organic bases. The ^{19}F spectra of the complexes are fully consistent with an octahedral model, and the P–F coupling constants, similar to that in PF_6^-, suggest a relative insensitivity of hybridization to the type of donor molecule. In accord with the strong acceptor properties, the pentafluoride is an excellent catalyst for ionic polymerizations. Especially noteworthy is the PF_5-catalysed polymerization of tetrahydrofuran to a very high ($M_n = 280{,}000$) molecular weight elastomer. Phosphorus trifluoride, unlike the pentafluoride, exhibits no significant acceptor properties. However, the trifluoride does undergo a curious disproportionation, $3MF + 5PF_3 \rightarrow 3MPF_6 + 2P$, that may involve an MPF_4 intermediate.

Synthesis

We have found that phosphorus fluorides can be prepared in high yield and purity directly from calcium fluoride and the phosphorus chlorides. Calcium fluoride reacts exothermally with PCl_5 at 300–500° to form $CaCl_2$ and PF_5. In a sealed reaction vessel (metal) and in a flow system (glass) wherein gaseous PCl_5 was carried in an inert gas, conversions of PCl_5 to PF_5 ranged from 85 to 98 per cent. Purities were estimated to range from 85 to 98 per cent. Principal impurities were POF_3 (and SiF_4 when reaction was effected in glass equipment) and chlorine. Chlorine was readily removed by treatment with sulphur trioxide. Similarly, PCl_3 and CaF_2 gave PF_3 in 77 per cent yield at 350°.

Phosphorus pentafluoride was also prepared in good yield by "chlorofluorination" of PF_3 with CaF_2 and chlorine at 350° in a sealed vessel. This chlorofluorination is probably complex since each of the steps outlined below are either known reactions or were demonstrated in this study:



Acceptor properties of PF_5

Phosphorus pentafluoride exhibits the general acceptor properties of the classic Lewis acid, BF_3. Complexes of PF_5 with such bases as ethers, sulphoxides, amines, amides and esters were prepared, and data for these complexes are listed in Table 1. The PF_5 complexes are much less stable than the analogous BF_3 complexes. For example, unlike the BF_3 amine complexes that can be recrystallized from water, all of the PF_5 complexes are decomposed rapidly by water and by alcohols. The relationship is the reverse to that which pertains in the hydrolytic stability of BF_4^- and

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PF_6^-. The lower stability of the PF_5 complexes may be due at least partially to steric factors, the importance of which is well established in BF_3 complexes.[1] The P^{5+} atom is only slightly larger than B^{3+} and yet must accommodate two more fluorine atoms in its complexes. Direct evidence for a steric factor was found in ether and amine complexes: $PF_5 \cdot O(C_2H_5)_2$ is largely dissociated at 25° whereas $PF_5 \cdot O(CH_2)_4$ can be distilled at 116°/0·15 mm. Two hindered amines, triethylamine and 2,4,6-trimethylpyridine, showed only partial association with PF_5 at 25°.

Evidence for the structure of the PF_5 complexes was obtained from the ^{19}F magnetic resonance spectra (40 Mc/s) of acetonitrile solutions of the sulphoxide, amine, oxime, amide and thioamide complexes. All of these consisted of two sets of a doublet and quintuplet of relative intensities four and one, respectively; the two sets arise from ^{31}P–^{19}F coupling. The doublet-quintuplet fine structure is the predicted pattern for an octahedral structure in which there are four equivalent, coplanar fluorine atoms and one apical fluorine atom. The ^{31}P–^{19}F coupling constants varied slightly (710–765 c/s) from complex to complex and averaged about 740 c/s, as compared to 710 c/s for PF_6^-. Since M–F coupling constants *appear* to reflect[2,3] the fractional *p* character of M–F hybrid bonds (only *p* electrons are effective in the coupling), the near identity of J_{P-F} in PF_6^- and PF_5·base *suggests* similar hybridization in these fluorides. The F–F coupling constants averaged about 55 c/s.

The doublet-quintuplet fine structure was not observed in the ^{19}F spectra of PF_5 dissolved in ethers, esters and nitriles; only a doublet was observed at 25°. In the case of $PF_5 \cdot (C_2H_5)_2O$ dissolved in ether, the expected pair of doublets (broadened) but not the pair of quintuplets were resolved at −78°. On warming, the doublets merged into single peaks. Loss of fine structure is attributed to the rapid equilibrium:

$$PF_5 + \text{base} \rightleftharpoons PF_5 \cdot \text{base}$$

that would yield effective equivalence of fluorine atoms and yet preserve ^{31}P–^{19}F coupling, because no P–F bonds are cleaved in this scheme. Such a rapid equilibrium is consistent with the very weak donor properties of the above-cited bases.

In accord with the strong acceptor properties of PF_5, the fluoride is an outstanding catalyst, particularly in ionic polymerizations. Examples of organic monomers readily polymerized are vinyl ethers and sulphides, isobutylene, styrene, butadiene, dihydropyran and epoxides. Phosphorus pentafluoride, unlike boron trifluoride, is especially effective for the polymerization of tetrahydrofuran. Bulk polymerization of tetrahydrofuran at 30° in the presence of PF_5 yielded very high molecular weight (M_n = 180,000–280,000) elastomeric solids. Phosphorus oxyfluoride is not a catalyst for these polymerizations.

Acceptor properties of PF_3

Arsenic and antimony trifluorides have been shown to function as Lewis acids by the formation of $MAsF_4$[4,5] and $MSbF_4$[6] salts and by formation of molecular complexes[6,7] with organic bases. Thus, phosphorus trifluoride was expected to exhibit

[1] H. C. Brown and co-workers, cf. H. C. Brown, *J. Chem. Soc.* 1248 (1956).
[2] H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.* **21**, 279 (1953).
[3] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.* **81**, 1084 (1959).
[4] A. A. Woolf and N. N. Greenwood, *J. Chem. Soc.* 2200 (1950).
[5] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.* **79**, 3686 (1957).
[6] H. J. Emeleus, *Fluorine Chemistry* Vol. 1, p. 55. Academic Press, New York (1950).
[7] A. Besson, *C.R. Acad. Sci., Paris* **110**, 1258 (1890); E. L. Muetterties. Unpublished work.

acceptor properties although to a lesser degree than the lower members of the Group V trifluorides. However, we could find no evidence for molecular complex formation and only indirect evidence for fluorophosphites.

Fluorophosphites had been previously suggested by several investigators.* We found that KF and CsF do, in fact, absorb PF_3 at ~150° but the product is not MPF_4 but a mixture of MPF_6 and red phosphorus. Thus, these alkali metal fluorides induce a rather remarkable low temperature disproportionation of PF_3 with formation of the very stable hexafluorophosphate salts the presumed driving force of the reaction:

$$3MF + 5PF_3 \rightarrow 3MPF_6 + 2P$$

This reaction may proceed through an MPF_4 intermediate.†

Phosphorus trifluoride is only slowly absorbed by water, a weak base, but it is rapidly absorbed by concentrated aqueous base. This attack by OH^- ion may well involve intitial formation of PF_3OH^-. However, attempts to detect intermediate fluorophosphites by following the ^{19}F spectrum (for appearance of a doublet due to ^{31}P–^{19}F coupling) of aqueous KOH solution during PF_3 absorption were unsuccessful; only fluoride ion was detected. Thus, fluorophosphites, if they exist, are hydrolytically unstable as is the tetrafluoroarsenite anion.[4]

Fluorine exchange

Several fluorides, AsF_3, SbF_3 and SbF_5, closely related to PF_3 and PF_5 show a marked tendency to undergo fast intermolecular exchange either in the pure state or with covalent fluorides.[3] However, we found, from nuclear magnetic resonance studies, that neither PF_3 nor PF_5 undergo fast exchange either in the pure state or in the presence of a number of fluorides that are known to catalyse fluorine exchange. A major distinction between PF_5 and SbF_5 and between PF_3 and AsF_3 or SbF_3 is the degree of molecular association; for example, PF_5 (b.p. −80°) is essentially non-associated whereas SbF_5 (b.p. 150°) is highly associated through fluorine bridge bonding. These properties and exchange behaviours are consistent with an earlier observation that there is some correlation between ease of intermolecular fluorine processes and the degree of molecular association in a fluoride.[3,12]

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EXPERIMENTAL

Materials and physical methods

Reagent grade calcium fluoride was dried at 300–500° before use. Commercial samples of phosphorus chlorides and chlorine were used directly without purification. The organic bases were purified by standard techniques. Tetrahydrofuran employed in the polymerization studies was refluxed over KOH, then over $LiAlH_4$ and was finally distilled from $LiAlH_4$ under an atmosphere of nitrogen immediately prior to use.

The nuclear magnetic resonance spectra were obtained with a Varian high resolution spectrometer and electromagnet at 40 Mc/s and 56·4 Mc/s and fields of ~7,500 and 14,000 gauss, respectively. For the fluorine exchange studies, the fluorides were sealed in quartz capillaries (2 mm i.d.).

* BERTHELOT[8] and MOISSAN[9] proposed that fluorophosphites are formed when PF_3 is absorbed by aqueous bases; however, no products were isolated or characterized.

† The fluorides, AsF_3[4,5], IF_5[10] and TeF_6[11] react exothermally with KF, RbF, and CsF to form $MAsF_4$, MIF_6 and M_2TeF_8 salts but none of these fluorides react with sodium fluoride even under forcing conditions. Similarly, we found that PF_3 will not react with sodium fluoride.

[8] M. BERTHELOT, *C.R. Acad. Sci., Paris* **100**, 81 (1885).
[9] H. MOISSAN, *C.R. Acad. Sci., Paris* **99**, 655 (1884).
[10] H. J. EMELIUS and A. G. SHARPE, *J. Chem. Soc.* 2206 (1949); E. L. MUETTERTIES, Unpublished work.
[11] E. L. MUETTERTIES, *J. Amer. Chem. Soc.* **79**, 1004 (1957).
[12] E. L. MUETTERTIES and W. D. PHILLIPS, *J. Amer. Chem. Soc.* **79**, 322 (1957).

Synthesis of PF_5 *and* PF_3

A "Hastelloy C"-lined pressure vessel was heated to 200–300°, evacuated, cooled and then charged with 80 g CaF_2 and 50 g PCl_5. The vessel was heated to 400° for 3 hr and then cooled. Volatile product was distilled directly into a cooled (−78°) stainless steel cylinder. Molecular weights derived from gas density of the crude product ranged from 115 to 121 (theory, 126). Removal of chlorine impurity by treatment of the gas with SO_2 raised the molecular weight values to ~124. The remaining impurities were largely POF_3 and SiF_4. Mass spectrometric analyses consistently gave low values for PF_5 content due to hydrolysis within the spectrometer. Analytical determination of phosphorus and fluorine indicated purities in the 92–98 per cent range. Conversions of PCl_5 to crude PF_5 in nine seperate runs ranged from 85–98 per cent.

A 64 mm Pyrex tube, 2½ ft. in length, was packed with 400 g of $\frac{3}{16}$ in. calcium fluoride pellets in the centre 7 in. section. The reactor system was then baked out in a split furnace at 400° for 12 hr. The entrance to the reactor was connected to a small flask fitted with a nitrogen gas inlet and filled with about 70 g of phosphorus pentachloride. To the exit end of the reactor was connected a cold trap and a gas bubbler. The cold trap was cooled with liquid nitrogen. A slow stream of nitrogen gas was then passed through the reactor while the flask containing the phosphorus pentachloride was heated to sublime the chloride into the reaction zone. The reaction was exothermic and the reaction mass temperature was maintained at about 400° by control of the furnace input and of the rate of flow of phosphorus pentachloride. The gaseous product was collected in a liquid nitrogen trap and, at the completion of the reaction, it was transferred to a stainless steel cylinder. In the course of the reaction the section of the Pyrex tube enclosing the reaction zone was slightly etched due to the reaction:

$$2PF_5 + SiO_2 \rightarrow 2POF_3 + SiF_4$$

In all of the runs, infra-red analysis indicated that the major product (ca. 80–90 per cent) was phosphorus pentafluoride. The only impurities indicated were phosphorus oxyfluoride and silicon tetrafluoride. A summary of four runs using the above procedure is given below:

Amount of PCl_5 sublimed (g)	Yield of crude PF_5(%)	Conversion of PCl_5 to crude PF_5(%)	Reaction time (hr)
98	68	64	6
65	87	63	1·33
70	98	98	1
100	98	98	1·25

Phosphorus trifluoride was prepared from PCl_3 and CaF_2. Reaction of PCl_3 (180 g) and excess CaF_2 (234 g) in a "Hastelloy C"-lined pressure vessel at 350° for 8 hr yielded ~107 per cent of the theoretical volatile product indicating incomplete reaction. The crude product was roughly separated and the low boiling fraction was distilled. About 89 g (77 per cent yield) of PF_3, boiling at −101°, was obtained.

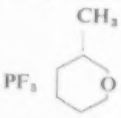
Chlorination and chlorofluorination of phosphorus trifluoride

Phosphorus trifluoride (30·2 g) and chlorine (24 g) were distilled into a 500 ml stainless steel cylinder which was cooled with liquid nitrogen. The mixture was then allowed to warm to room temperature over a period of about 30 min while the cylinder was slowly rotated. An exothermic reaction was not detected. In 24 hr, it was apparent that much of the product in the reaction was a solid. The cylinder was allowed to stand for a further period of five days and then was evacuated to about 1 mm pressure. The cylinder was opened and found to contain 47·7 g of a white solid that fumed in air and analysed approximately for a mixture of $PCl_4^+PF_6^-$ [13] (or $PCl_4^+F^-$ *. The ^{19}F magnetic resonance spectrum of a pyridine solution of this solid consisted of a doublet that was identical to that of PF_6^- (NH_4PF_6 solution).[2]

* KOLDITZ[14] has reported $PCl_4^+F^-$ to be a product of the thermal decomposition of $PCl_4^+PF_6^-$.

[13] L. KOLDITZ, *Z. Anorg. Chem.* **284**, 144 (1956).
[14] L. KOLDITZ, *Z. Anorg. Chem.* **286**, 307 (1956).

TABLE 1.—PF_5 COMPLEXES

Adduct	Analytical data											
	Carbon (%)		Hydrogen (%)		Phosphorus (%)		Fluorine (%)		Nitrogen (%)		m.p.(°C)	b.p.(°C)
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found		
$PF_5 \cdot (CH_3)_3N$	19·47	20·08	4·90	5·09	16·74	16·50	51·33	51·69	7·57	7·82	214–215	$170^{0\cdot 15\,mm}$
$PF_5 \cdot C_5H_5N$	29·28	29·94	2·46	2·94	15·11	13·62	46·32	46·61	6·83	7·27	179–182	
$PF_5 \cdot (CH_3)_2NCHO$	18·01	18·13	3·54	3·69	15·56	15·27	47·72	47·51	7·04	7·31	118–120	$50^{<1\,mm}$
$PF_5 \cdot (CH_3)_2NCHS$	16·74	16·88	3·28	3·70	14·40	14·03	—	—	6·51	6·50	190 d	
$PF_5 \cdot (CH_3)_2CNOH$	18·01	18·36	3·54	3·87	15·56	14·99	47·72	46·33	—	—	d	
$PF_5 \cdot (CH_3)_2SO$	11·77	13·65	2·96	3·55	14·75	15·14	46·54	45·78	15·71 (S)	16·37 (S)	d	
$PF_5 \cdot (C_2H_5)_2O$	—	—	—	(0·958:1·00 PF_5:$(C_2H_5)_2O$ at 5°)					—	—	—	dis.
$PF_5 \cdot (CH_2)_4O$	24·25	24·49	4·08	5·62	—	—	—	—	—	—	55	$116–118^{0\cdot 15\,mm}$
$PF_5 \cdot (CH_2)_5O$				(~1:1 PF_5:$(CH_2)_5O$ at 25°)							45–46	dis.
				(~1:1 PF_5:$C_5H_{10}O$ at 25°)								$70–80^{80\,mm}$ (dis.)

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In an attempt to isolate the molecular species PF_3Cl_2, the above procedure was followed except that immediately after mixing the product was transferred to a low temperature still. Distillation covering the period of 2·5 hr produced the following fractions: (1) 25 weight per cent b.p. −40–0°, (2) 70 weight per cent b.p. 0–5°, and (3) 5 weight per cent of liquid residue. Fraction (2) corresponded approximately in boiling point to the literature value for PF_3Cl_2 but its boiling point dropped slowly at total reflux suggesting that slow disproportionation was occuring in the still.

The PF_3–Cl_2 reaction was also examined by following the pressure as a function of time (Table 2, 0·52 mole of each reagent at 25° in a 500 ml stainless steel vessel).

TABLE 2.—PF_3-Cl REACTION

Time (hr)	Pressure (atm)	Non-volatiles weight (%)
0·5	2·9	—
1	3·0	<1
2	3·3	—
19	6·1	39
45	7·5	76
65	6·9	79
90	6·6	81
115	6·4	81
140	6·3	82

These data may be interpreted in terms of a very fast reaction of PF_3 and Cl_2 to give PF_3Cl_2 followed by two slow reactions, one that leads to a pressure decrease,

$$2PF_3Cl_2(l) \rightarrow PCl_4^+PF_6^-(c)$$

and one that gives a pressure increase,

$$2PF_3Cl_2(l) \rightarrow PCl_5(c) + PF_5(g)$$

At the end of 140 hr, the volatile fraction was essentially all PF_5, and the solid, non-volatile product was largely $PCl_4^+PF_6^-$ with small amounts of PCl_5 or $PCl_4^+F^-$.

A mixture of 81·2 g of PF_3, 65·5 g of Cl_2 and 123 g of CaF_2 was charged into a 1 l., Hastelloy rocker pressure vessel and heated for 8 hr at 350°.[15] The gaseous product weighed 116 g and its density corresponded to an average molecular weight of 115 (theory for PF_5, 126). Elemental analysis of the gas indicated a halogen–phosphorus ratio of 4·95:1 and a fluorine–chlorine ratio of 19:1. The product was largely phosphorus pentafluoride that contained chlorine impurities.

Preparation of PF_5 *complexes*

The complexes of PF_5 with nitrogen or sulphur organic bases were prepared by passing phosphorus pentafluoride slowly into a solution of the base in toluene. In some cases a precipitate was formed immediately and, in others, concentration of the toluene solution was necessary before a significant amount of crystalline complex separated out. In most instances, the complexes were recrystallized from tetrahydrofuran, dimethoxyethane or acetonitrile. The tetrahydrofuran complex[16] was prepared by passing phosphorus pentafluoride into tetrahydrofuran while the reaction mass was maintained at 0°. At about the point at which saturation of the tetrahydrofuran occurred, a solid product was formed. This material was then transferred under nitrogen to a vacuum sublimator whose cold finger was maintained near −40°, and with a vacuum of approximately 0·02 to 0·05 mm, the complex sublimed at about 70°. The analytical data and physical properties for these complexes are listed in Table 1. Some complexes were characterized only by the stoicheiometry of the PF_5·base reaction; there were $PF_5 \cdot S(CH_2)_4$, $PF_5 \cdot CH_3COOC_2H_5$, $PF_5 \cdot CH_3CN$, and $2PF_5 \cdot N_2O_4$. Stoicheiometries were determined in a vacuum system by reacting a known volume of PF_5 gas with a weighed

[15] E. L. MUETTERTIES, U.S. Pat. 2810629.
[16] E. L. MUETTERTIES, U.S. Pat. 2748145.

amount of liquid base. The decrease in pressure of the phosphorus pentafluoride (within a known volume of the vacuum system) then gave a rough measure of the stoicheiometry of the reaction.

The ease of protonic attack of all the PF_3 complexes was indicated by the observation that (1) molecular weight determinations in water (cryoscopic) and alcohol (ebulliometric) gave values that were fractions of the theoretical value and (2) the ^{19}F spectra in water and ethanol did not show the fine structure exhibited in acetonitrile solutions. The complexes were not soluble in benzene but molecular weight determination in acetonitrile (ebulliometric) indicated the complexes were simple molecular species, e.g. $PF_5 \cdot (CH_3)_2NCHS$, found, 218, calc., 215; $PF_5 \cdot N(CH_3)_3$, found, 199, calc., 185; and $PF_5 \cdot (CH_3)_2NCHO$, found, 182, calc., 199.

Mr. A. L. BIDDLE of this laboratory indexed the $PF_5 \cdot C_5H_5N$ complex as tetragonal with the parameters $a_0 = 13{\cdot}70$ Å, $c_0 = 11{\cdot}58$ Å, $c/a = 0{\cdot}845$, and $z = 8$.

Phosphorus oxyfluoride was found to be, at best, a very weak acceptor molecule. This fluoride gave very little heat of reaction (or solution) with typical organic bases. At 25°, the solubility of POF_3 in dimethylformamide and in dimethylsulphoxide is very low (5 per cent or less).

Reactions of PF_3

The solubility of PF_3 in organic bases was determined in a vacuum system at ~600 mm PF_3 partial pressure and 25°, and the values obtained for dimethyl sulphoxide, dimethylformamide and pyridine were, respectively, 0·01, 0·03, and 0·05 mole/mole of solvent. The ^{19}F spectrum of a mixed solution of pyridine and liquid PF_3 gave the characteristic PF_3 spectrum; there was no significant perturbation of the ^{31}P–^{19}F coupling constant. Equimolar amounts of pyridine and PF_3 were heated in a stainless steel-lined pressure vessel for 2 hr and these components were recovered unreacted.

Cesium fluoride in contact with an atmosphere of PF_3 in a vacuum system began to slowly absorb the trifluoride at about 130°. Potassium fluoride behaved similarly. X-ray investigation of the solid products indicated the presence of the corresponding metal hexafluorophosphates. The solid products when dissolved in water and filtered yielded a red-brown, insoluble material that proved by the nature of its combustion and by the odor of the combustion products to be amorphous red phosphorus. The filtrate yielded a precipitate with nitron acetate that analytical data indicated to be nitron hexafluorophosphate. (Found: C, 53·71; H, 3·74. Calc. for $C_{20}H_{16}N_4HPF_6$: C, 52·41 H, 4·03%).

This disproportionation reaction was not driven to completion even in pressure vessels at 250°, presumably because the red phosphorus coated the surface of the unreacted metal fluoride. Sodium fluoride showed no evidence of reaction with the trifluoride in a sealed reactor at temperatures as high as 280° (5 hr reaction period).

Polymerization of tetrahydrofuran

Phosphorus pentafluoride or the phosphorus pentafluoride-tetrahydrofuran complex readily initiated the polymerization of tetrahydrofuran at temperatures of 10–30°.[17] Uniform conversions to polymer of 60–70 per cent were obtained over a time range of 1–18 hr but molecular weights were usually at a maximum after a period of 5–7 hr. A typical example of a bulk polymerization is as follows: Tetrahydrofuran (89 g) containing the PF_3–tetrahydrofuran complex (0·24 g) was maintained at 30° for 6 hr under a nitrogen atmosphere. The viscosity rapidly increased and the material gave no evidence of flow after 1·5 hr. The resultant product was heated in water to destroy the catalyst and was then dissolved in tetrahydrofuran and slowly added to ice water in a Waring Blendor. The polymer separated out as a white, shredded solid (60 per cent conversion, inherent viscosity 3·94). High molecular weight polytetrahydrofuran samples usually showed block melting points greater than 150° and ranged as high as 215°. True crystalline melting points of 40–47°, as indicated by the disappearance of polymer crystallites to give amorphous material, were obtained by use of both the X-ray and polarizing hot-stage microscope methods. If 45° is taken as a representative crystalline melting point and if the empirical relationship, $T_g = \frac{2}{3} T_{mp} - 90$ (in °C), between the amorphous transition temperature and the crystalline melting point is used, one obtains a calculated value of −60° for the amorphous transition temperature. Natural rubber and neoprene have values of −72° and −40°, respectively. Thus, polytetrahydrofuran would appear to be inherently a rubbery polymer. The very high block melting points, in the range 150–200°, reflect primarily the high melt viscosity of the higher molecular weight polymers.

[17] E. L. MUETTERTIES, U.S. Pat. 2856370.

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Fluorine exchange

Fast intermolecular exchange processes lead to collapse of fine structure in nuclear magnetic resonance spectra. This criterion was employed to detect exchange in PF_5 and PF_3. Neither PF_5 nor PF_3 were found to undergo fast (10^3 sec^{-1}) intermolecular fluorine exchange in the pure liquid state. In the ^{19}F spectra, the ^{31}P–^{19}F coupling is not lost in liquid PF_5 or PF_3 up to the critical temperature (estimated T_c: $\sim 15°$, PF_5 and $\sim -15°$, PF_3). The coupling is also preserved in the gaseous state at 30° in both fluorides. Retention of ^{31}P–^{19}F coupling was also observed in liquid or gaseous PF_3 when this fluoride was in contact with PF_5 (*l*), AsF_3 (*c*) or (*l*), CsF (*c*), BF_3 (*l*), or SF_4 (*l*). The same was true for PF_5 in contact with PF_3 (*t*), AsF_3 (*c*) or (*l*), $CsPF_6$ (*c*), BF_3 (*l*), IF_5* (*c*) or (*l*), or SF_4PF_6 (*c*).

* Liquid IF_5 (an associated liquid) and liquid PF_5 are not miscible.

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TRI- AND TETRA-MERIC PHOSPHONITRIDIC FLUORIDE*

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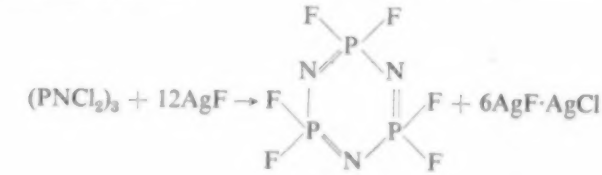
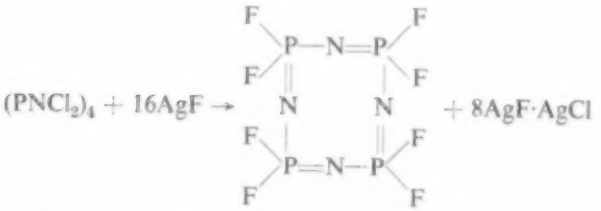
Abstract—The tri- and tetra-meric phosphonitridic fluoride $(PNF_2)_3$ and $(PNF_2)_4$, respectively, can be easily obtained in satisfactory yields by reacting the corresponding phosphonitridic chlorides with argentous fluoride. The mass spectrum proves the assumed cyclic structure for both compounds.

VARIOUS attempts have been made to convert the phosphonitridic chlorides into the corresponding fluorides by means of reactions with various metal fluorides. The only attempt, so far successful, was recently reported by SEEL[1], while this investigation was in progress. SEEL used potassium fluoro sulphinate, KSO_2F, a novel fluorinating agent. In our laboratory it was observed that the use of commercially available argentous fluoride exchanges all chlorine functions in $(PNCl_2)_{3\ or\ 4}$ by fluorine in accordance with the following equations:



$$(PNCl_2)_3 + 12AgF \rightarrow (PNF_2)_3 + 6AgF{\cdot}AgCl \qquad (a)$$



$$(PNCl_2)_4 + 16AgF \rightarrow (PNF_2)_4 + 8AgF{\cdot}AgCl \qquad (b)$$

Contrary to other heavy metal fluorides, argentous fluoride did not cause any cleavage of the —P=N— bonds or a change in the size of the molecule. Such a ring enlargement from the 6-membered P=N— ring to the 8-membered —P=N—ring was reported earlier in the case of lead fluoride (PbF_2) by SCHMITZ-DU MONT and KÜLKENS[2].

For the complete fluorination of the polymeric phosphonitridic chlorides by means of argentous fluoride at least 4·5–5·0 moles of argentous fluoride per $P:Cl_2$ group were necessary because the first formed AgF·AgCl did not take part in the succeeding reaction. Since SCHMITZ-DU MONT and KÜLKENS[2] applied only 2 moles of AgF/

* This article is based on work performed in 1956 and 1957 under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corporation, New Haven, Connecticut.
‡ Olin Mathieson Chemical Corporation, New Haven, Connecticut.
§ General Cigar Co., Inc., Lancaster Pennsylvania.

[1] F. SEEL, *Angew. Chem.* **68**, 461 (1956).
[2] O. SCHMITZ-DU MONT and H. KÜLKENS, *Z. Anorg. Chem.* **238**, 189 (1938).

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$P:Cl_2$ group, they were unsuccessful in the isolation of the desired phosphonitridic fluorides. The reaction of the various phosphonitridic chlorides with argentous fluoride was carried out without application of a solvent or diluent. However, the fluorination-reaction took place partially also in refluxing acetonitrile as a solvent, but in this case the separation of the highly volatile phosphonitridic chlorofluorides could not be achieved satisfactorily. The fluorination proceeded stepwise, and it was possible to obtain under certain conditions partially fluorinated compounds. In the case of the trimeric phosphonitridic chloride the isolation and identification of phosphonitridic dichloro-tetrafluoride ($P_3N_3Cl_2F_4$) with the same ring size as the starting material could be achieved.

The physical properties of $(PNF_2)_3$ and $(PNF_2)_4$ were found to be in excellent agreement with the data given by SEEL[1]. $(PNF_2)_3$ synthesized by the silver fluoride procedure melted at 28°, the boiling point at atmospheric pressure was observed to be 52°. The corresponding values of the tetramer are 30·5° and 90°, respectively.

The trimeric phosphonitridic dichloro-tetrafluoride is a colourless liquid, $b.p._{(740\ mm)}$: 106–109°. The two chlorine atoms in this compound could be exchanged by fluorine by means of argentous fluoride as well as argentic fluoride (AgF_2). Attempted fluorination of the non-fluorine-containing phosphonitridic chlorides by means of argentic fluoride led to excessive degradation.

The molecular size of $(PNF_2)_3$ and $(PNF_2)_4$ could be proved by mass-spectroscopy. The spectra were produced at 70, 14 and 12 V accelerating potential. These spectra are quite well in agreement with cyclic formulae shown in equations (a) and (b). The interesting point about both spectra are the very large parent peaks at m/e 249 and m/e 332. In addition to the many fragment peaks, such as $P_3N_3F_5^+$ in the trimer as well as PF_2^+ and $P_4N_4F_7^+$ in the tetramer, both samples contained according to the mass spectra a trace amount of the chloro-fluorides $P_3N_3F_5Cl$ and $P_4N_4F_7Cl$. However, by conventional analytical methods it was impossible to detect any chlorine in $(PNF_2)_3$ and $(PNF_2)_4$ produced by the argentous fluoride method. The infra-red spectrum of $(PNF_2)_3$ was determined in carbon tetrachloride and carbon disulphide solutions in the ratio 0·05 g to 1 ml solvent. Strong absorption peaks at 7·75 μ (*vs*), 10·31 μ (*vs*), 11·55 μ (*vs*), 11·73 μ (*vs*), and 12·78 μ (*vs*) were observed for the trimer. However, no absorption band was found at 8·22 μ (1218 cm^{-1}), assigned by DAASCH[3] to the P_3N_3 ring system. Tentatively, the fluorine atoms cause a shift of this absorption to shorter wavelength.

The infra-red spectrum of $(PNF_2)_4$ was determined in carbon tetrachloride and carbon disulphide in the ratio 0·05 g to 1 ml solvent. Strong absorption peaks were observed at 7·05 μ (*vs*), 10·31 μ (*vs*) and 13·17 μ (*vs*).

EXPERIMENTAL

Trimeric phosphonitridic fluoride $(PNF_2)_3$. In a 500 ml two-neck glass flask connected with a reflux condenser, pure, finely ground trimeric phosphonitridic chloride (34·8 g = 0·1 mole) was mixed with 132 g (1·05 mols) of pulverized argentous fluoride. The condenser was cooled with ice-water. The reaction was started by slowly warming the mixture to 80–90°C by means of an oil-bath. At this temperature the main reaction took place, making it necessary to remove the oil-bath for some minutes. To complete the reaction the liquid part of the mixture was then refluxed for 4 hr in an oil-bath at 140°C. After standing overnight, the condenser was exchanged for a sausage receiver which was cooled to −40°C by powered Dry-Ice. The separation of the reaction product from the

[3] L. W. DAASCH, *J. Amer. Chem. Soc.* **76**, 3403 (1954).

silver salts was achieved by distillation from an oil-bath at 130°C, first under atmospheric pressure, finally at 10 mm pressure. A water-clear mobile liquid (22 g) was obtained, which was not uniform, but a mixture of still impure trimeric phosphonitridic fluoride and several different phosphonitridic chlorofluorides. The liquid was distilled at atmospheric pressure between 50 and 115°C. The liquid mixture of phosphonitridic chlorofluorides (22 g) was refluxed again with 15 g of fresh argentous fluoride in an oil-bath at 110–125°C. After 12 hr the $(PNF_2)_3$ started to crystallize in rhombic crystals in the lower part of the reflux condenser. By continuous refluxing with additional 20 g of argentous fluoride all of the formed product could be separated from the reaction mixture in this manner. After 48 hr 8·5–10 g of high purity $(PNF_2)_3$ was obtained by scraping the hard crystals out of the condenser with a metal spatula. Yield: 34·5–40·5%, b.p.$_{(750\ mm)}$: 51·8–52°C, m.p. 28°C. (Thiele apparatus, sealed capillary.)

Further fluorination of the phosphonitridic chlorofluoride mixture was also achieved by means of argentic fluoride. Thus, an amount of 10 g of the liquid mixture was mixed at room temperature with 2 g-portions of 12 g of argentic fluoride, allowing each portion to react completely at 110°C before adding the next one. After 4 hr all fluorinating agent was added and the mixture finally refluxed for 3 hr at 125°C. The formed $(PNF_2)_3$ crystallized almost quantitatively in the lower part of the condenser. Yield: 4·4 g, b.p.$_{(750\ mm)}$: 52°C, m.p. 28°C. (Found: P, 36·04, 35·95; N, 16·40, 16·22; F, 45·47, 45·42. Calc. for $P_3N_3F_6$: P, 37·31; N, 16·88; F, 45·81%).

Compared with the calculated value, the observed P values were somewhat low. A similar observation was made also on trimeric phosphonitridic bromochlorides, prepared recently by RICE and DAASCH[4].

Trimeric phosphonitridic dichlorotetrafluoride. This compound was obtained by fractional distillation of the forementioned liquid mixture boiling between 50 and 115°C. An amount of 22 g of this mixture gave on distillation at atmospheric pressure 5 g of pure $P_3N_3F_4Cl_2$, b.p.$_{(740\ mm)}$: 106–109°C, n_D^{26} 1·4055. (Found: P, 33·04, 33·28; Cl, 25·17, 25·18. Calc. for $P_3N_3Cl_2F_4$: P, 32·97; Cl, 25·15%).

Tetrameric phosphonitridic fluoride $(PNF_2)_4$. A mixture of tetrameric phosphonitridic chloride (23·2 g = 0·05 mole) and argentous fluoride (100 g = ~0·80 mole), both finely pulverized, was reacted in the same manner as described for $(PNF_2)_3$. A strong exothermic reaction started at 135°C oil-bath temperature. After 2 hr refluxing followed by standing overnight, 10 g of a liquid reaction product was separated from the silver salts by vacuum distillation at 160°C (3 mm). A sausage adapter cooled with Dry-Ice was used as a receiver. In addition to the 10 g of liquid product, 3 g of unreacted starting material was recovered, boiling at 180°C (3 mm). The liquid reaction product (10 g) was then refluxed with the equal amount of fresh AgF. After 6 hr the first compact crystals of $(PNF_2)_4$ appeared in the lower part of the condenser. After 12 hr the remaining liquid was vacuum-distilled into a Dry-Ice cooled sausage receiver. Repeated fluorinations of this liquid product with 8 g and finally with 6 g of fresh argentous fluoride resulted in an overall yield of 5·75 g of $(PNF_2)_4$ = 40 per cent; b.p.$_{(740\ mm)}$: 89·5–90·3°C, m.p. 30°C. (Found: P, 36·28, 36·14; N, 16·22, 16·11; F, 45·57, 45·55. Calc. for $P_4N_4F_8$: P, 37·31; N, 16·88; F, 45·81%).

Acknowledgements—The authors are very much indebted to the Olin Mathieson Chemical Corporation for the generous support of this investigation. We are also indebted to Dr. J. H. NORMAN, Olin Mathieson Chemical Corporation, Niagara Falls, N.Y. for the mass-spectroscopical work and for the interpretation of the spectra. Furthermore we want to express our indebtedness to Miss D. M. ROBINS, Olin Mathieson Chemical Corporation, Niagara Falls, N.Y. for the determination of the infra-red spectra.

[4] R. G. RICE and L. W. DAASCH, *J. Inorg. Nucl. Chem.* **5**, 190 (1958).

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PREPARATION OF N,N-DIFLUOROMETHYLAMINE AND N,N-DIFLUOROETHYLAMINE*

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Abstract—A method is described for the preparation of N,N-difluoromethylamine and N,N-difluoroethylamine. Some of the physical properties of these compounds are listed.

THE compounds N,N-difluoromethylamine and N,N-difluoroethylamine are of interest in that they are the first of a homologous series containing difluoroamino (NF_2) groups. The synthesis method itself is of interest in that it may be of general use in the introduction of a NF_2 group into an organic compound. The preparation involves the reaction of CH_3I or C_2H_5I with N_2F_4 when subjected to ultra-violet excitation ($\geqslant$2750 Å).

The N_2F_4 was prepared by the mercury discharge method.[1] Purification was accomplished by chromatographic techniques using a 7 ft silica gel column at −55°C.

The reactants, N_2F_4 and reagent-grade CH_3I or C_2H_5I, were contained in a Pyrex flask at a fixed distance from a 350-watt low-pressure mercury arc. The temperature of the reactants was not controlled and varied between 25° and 40°C. Purification of the CH_3NF_2 and $C_2H_5NF_2$ from unreacted starting materials and other products was by chromatography.

The chromatography columns were $\frac{1}{4}$ in. o.d. copper tubes. Packing materials were made from 15 g of the appropriate liquid phase per 100 g of 60–80 mesh Johns-Manville C-22 firebrick.

CH_3NF_2 *synthesis*

Reaction (1) was found to proceed very slowly when the compounds

$$CH_3I + N_2F_4 \rightarrow CH_3NF_2 + \ldots . \quad (1)$$

were placed in a Pyrex container in sunlight. When the same procedure was followed using the 350 W ultra-violet source, a reasonable reaction rate was obtained. The yield of CH_3NF_2 and other products were dependent upon the ratio and pressure of the reactants. In all systems examined HCN, HNF_2, I_2 and SiF_4 were formed. When the reaction was continued for several days ICN was also formed.

The results as shown in Table 1 are from 20 hr runs where the reaction vessels were placed at a distance of 11 in. from the ultra-violet source.

At a given starting pressure of N_2F_4 the HCN yield drops as the pressure of CH_3I is increased. This suggests that the CH_3NF_2 as first formed is not in the ground state. It is thought that the excited CH_3NF_2 can lose energy by collisions or by dehydrofluorination (2).

$$CH_3NF_2 \rightarrow HCN + 2HF \quad (2)$$

* Work was done under auspices of the U.S. Atomic Energy Commission.

[1] J. W. FRAZER, *J. Inorg. Nucl. Chem.* **11**, 166 (1959).

TABLE 1.—CH_3NF_2 YIELD DATA

N_2F_4 pressure (cm)	CH_3I pressure (cm)	CH_3NF_2* yield (%)	HCN* yield (%)	HNF_2* yield (%)	% Completion of reaction (1)
2·59	2·59	4	>20	trace	12
2·59	12·9	35	5–10	~1	50
2·59	25·9	50	2–4	~4	64
30·5	30·5	52	15	~2·5	34

* Yield data is based on the amount of N_2F_4 reacted.

It was found that CH_3NF_2 is very stable under the conditions used for the reaction. Purified CH_3NF_2 was irradiated in Pyrex for 19 hr at a distance of 10 in. from the ultra-violet source. No reaction occurred as determined by infra-red spectroscopy. When heated in a Pyrex bomb for 1 hr 40 min at 120°C, no change could be detected as determined by mass spectrometer data.

Purification of the CH_3NF_2 was by chromatography at room temperature. The initial separation was made on a 10 ft di-n-decyl phthalate column. This was followed by a final purification using a 30 ft oxydipropyl nitrile column. The 10 ft di-n-decyl

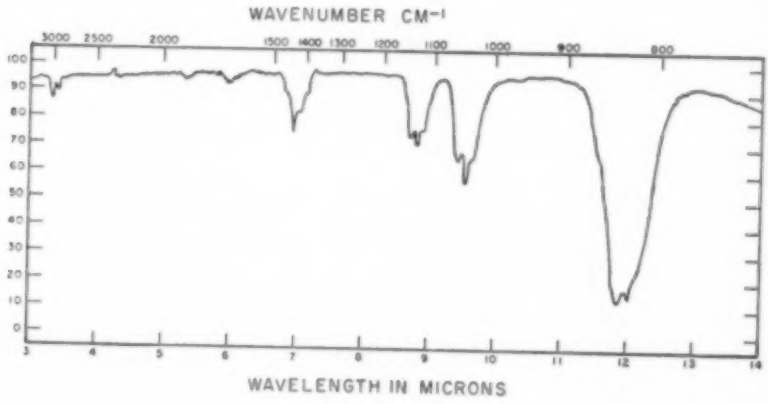

FIG. 1.

phthalate column separated the CH_3NF_2 from all the aforementioned contaminants. However, there is often a small contaminant (<0·1 per cent) having an apparent molecular weight of ninety-six as determined by mass spectrum data. This compound, can not be separated from the CH_3NF_2 on the first column and therefore another purification is needed using the 30 ft oxydipropyl nitrile column. The compound might be of interest, but all attempts to synthesize it in larger quantities have failed. Mass spectrometer and infra-red data appear to be consistent with a compound such as $CH_3NFNF\,CH_3$.

Final purification of the CH_3NF_2 was by a trap-to-trap distillation retaining the −95° to −130°C cut. This distillation was necessary to remove traces of air and water. Purity and identification were based on molecular weight, mass (Table 2) and infra-red (Fig. 1) spectra. The molecular weight was determined by the technique of limiting densities; calculated 67·04, found 66·97.

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TABLE 2.—MASS SPECTRUM DATA FOR CH_3NF_2

m/e	Ion assignment	Pattern (%)
15	CH_3^+	100
27	HCN^+	15·8
28	CH_2N^+	79·5
29	CH_2N^+	5·6
33	NF^+	4·3
46	$CHNF^+$	8·4
47	CH_2NF^+	3·6
66	$CH_3NF_2^+$	5·5
67	$CH_2NF_2^+$	35·4

Some of the physical properties of CH_3NF_2 are listed below. The vapour-pressure over the range $-69{\cdot}0°$ to $-19{\cdot}3°C$ can be expressed by (3).

$$\log_{10} P = 5{\cdot}6731 - \frac{755{\cdot}13}{T} - \frac{56631}{T^2} \tag{3}$$

where P is the pressure in centimetres of Hg and T is the temperature in degrees Kelvin. The temperature was determined to $\pm 0{\cdot}15°C$ and the pressure to $\pm 0{\cdot}005$ cm.

Boiling point (760 mm) $= -16{\cdot}0° \pm 0{\cdot}1°C$
Melting point $= -114{\cdot}8 \pm 0{\cdot}3°C$
Density $= 1{\cdot}099 \pm 0{\cdot}0005$ g/cm³ at $-20°C$
Latent heat of vaporization at the boiling point = 5·48 kcal/mole

$C_2H_5NF_2$ *synthesis*

The reaction

$$C_2H_5I + N_2F_4 \rightarrow C_2H_5NF_2 + \ldots . \tag{4}$$

was carried out in much the same manner as reaction (1). The reactants were contained in Pyrex flasks for 15 hr at a distance of 11 in. from the ultra-violet source. Yield data are shown in Table 3.

TABLE 3.—$C_2H_5NF_2$ YIELD DATA

N_2F_4 pressure (cm)	C_2H_5I pressure (cm)	N_2F_4 consumed (%)	% Yield of $C_2H_5NF_2$
1·7	1·7	12	60
1·7	3·4	19	61
1·7	10·2	80	70

Other reaction products were a trace of HCN and small percentages of HNF_2 and SiF_4. In addition, there was <0·1 per cent of an unknown product.

Purification was by gas chromatography using a 25 ft di-n-decyl phthalate column at room temperature. A final purification was made by a trap-to-trap distillation retaining the $-95°$ to $-130°C$ cut.

Purity was again based on molecular weight determinations; found 81·08, calculated 81·07. Confirmation of these results was by data obtained from the mass (Table 4) and infra-red (Fig. 2) spectra.

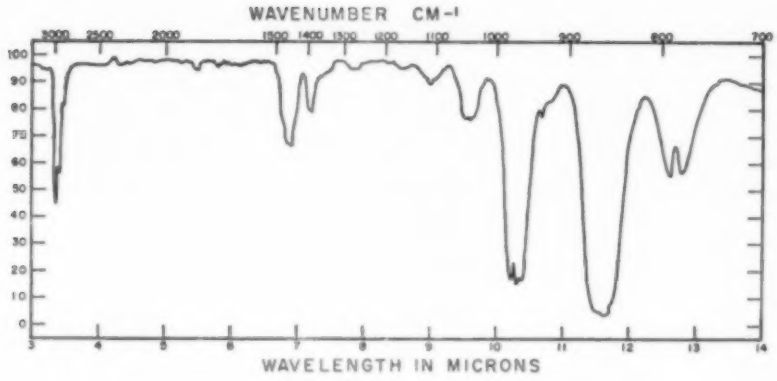

FIG. 2.

TABLE 4.—MASS SPECTRUM DATA FOR $C_2H_5NF_2$

m/e	Ion assignment	Pattern (%)
15	CH_3^+	36·2
27	$C_2H_3^+$	70·6
28	$C_2H_4^+$	20·8
29	$C_2H_5^+$	100·0
33	NF^+	3·2
43	$C_2H_5N^+$	7·5
66	$CH_3NF_2^+$	3·8
81	$C_2H_5NF_2^+$	0·8

Some of the physical properties of $C_2H_5NF_2$ are given below. The vapour pressure over the range $-32{\cdot}0°$ to $-14{\cdot}4°C$ can be expressed by

$$\log_{10} P = 5{\cdot}7005 - \frac{856{\cdot}30}{T} - \frac{70345}{T^2} \tag{5}$$

where P is the pressure in centimetres of Hg and T is the temperature in degrees Kelvin. Temperature measurements were made to $\pm 0{\cdot}1°C$ and the pressure was measured to $\pm 0{\cdot}005$ cm.

Boiling point $= 14{\cdot}9° \pm 0{\cdot}1°C$
Melting point $= -150{\cdot}3 \pm 0{\cdot}3°C$

The density can be expressed by

$$\log_{10} D = -0{\cdot}41505 + \frac{177{\cdot}14}{T} - \frac{16889}{T^2} \tag{6}$$

over the range $-34{\cdot}8°$ to $-14{\cdot}7°C$. D is the density in g/cm³ and T is the temperature in degrees Kelvin. The density at 0°C is 1·0165 g/cm³.

Latent heat of vaporization at the boiling point = 6·14 kcal/mole

Care should be exercised in the handling of these materials as they are undoubtedly shock sensitive. In addition, they should be stored as pure compounds to insure their stability. It has been found that the decomposition of compounds containing (NF_2) groups are very often auto-catalytic.

Acknowledgement—The author wishes to express his appreciation to V. DU VAL for his help in determining some of the physical properties and to C. J. DOOLEY for the mass spectra data.

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ÜBER DEN SCHMELZPUNKT UND DIE THERMISCHE DISSOZIATION VON TITANDIOXYD

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Abstract—The behaviour of titanium dioxide has been investigated at temperatures up to the melting point. The oxide loses oxygen on heating. The solid residue consists of a non-stoicheiometric compound of the composition TiO_{2-x}. The value of the coefficient x depends on the temperature and the oxygen pressure of the gaseous phase. In addition the melting points of TiO_2 and Ti_2O_3 have been determined, and the liquidus curve of the system TiO_2–Ti_2O_3 has been measured. For the measurements of the melting points a method, using a sun-mirror has been developed with which temperatures up to 3000°C can be obtained in any gaseous atmosphere.

DIE THERMISCHE DISSOZIATION VON TITANDIOXYD

VON den drei bekannten Modifikationen des Titandioxyds TiO_2 ist allein der Rutil von Zimmertemperatur bis zum Schmelzpunkt beständig. Er spaltet jedoch beim Erhitzen an Luft, im Vakuum oder in neutraler Gasatmosphäre Sauerstoff ab. Die Sauerstoffabgabe nimmt mit der Temperatur zu und erreicht gut messbare Beträge erst in der Nähe des Schmelzpunktes. Die thermische Dissoziation gemäss

$$2TiO_2 = 2TiO_{2-x} + xO_2$$

kann durch optische und elektrische Erscheinungen nachgewiesen werden, wie im folgenden kurz dargelegt wird.

TiO_2 verwandelt sich beim Glühen in gefärbte Produkte mit Farbtönungen, die bei einer von 1400 bis 1800°C ansteigenden Glühtemperatur von grau über dunkelblau bis schwarz variieren.

Aus Untersuchungen der elektrischen Leitfähigkeit an Titandioxyd bei Temperaturen im Bereich zwischen 100°C und 1200°C lässt sich für jede einzelne Temperatur feststellen, dass mit abnehmendem Sauerstoffdruck der die Probe umgebenden Atmosphäre der spezifische elektrische Widerstand abnimmt, d.h. die Leitfähigkeit ansteigt. Die Zunahme der Leitfähigkeit ist ihrerseits wieder mit der Zunahme der Zahl oder der Beweglichkeit von Leitungselektronen* pro Volumeneinheit des vorliegenden Oxyds gekoppelt. Diese Zunahme an Leitungselektronen mit steigender Temperatur oder abnehmendem Sauerstoffgehalt der Gasatmosphäre ist offenbar durch eine Abweichung des Titandioxyds von seiner ganzzahlig stöchiometrischen Zusammensetzung im Sinne eines Sauerstoffdefizits durch Sauerstoffabspaltung bedingt. Gleichzeitig entstehen und vermehren sich in der nichtdaltoniden Verbindung TiO_{2-x} die Pohl-Schottky'schen F-Zentren, die für die zunehmende Färbung des Oxyds, d.h. für die Änderung der Lichtabsorption verantwortlich sind.

* Es handelt sich hierbei nicht um Ionenleitfähigkeit, sondern, wie eigene Untersuchungen der Halbleitereigenschaften an den Kristallpulvern ergaben, um Elektronenüberschussleitung vom n-Typ.

BISHER DURCHGEFÜHRTE SCHMELZPUNKTSBESTIMMUNGEN AN TITANDIOXYD

Die bis jetzt bekannten Daten für die Schmelztemperatur von TiO_2 liegen im Bereich zwischen 1560 und 1900°C.[1–11]

Nach unseren eigenen neuesten Erfahrungen sind all diese Werte immer noch mit der Unsicherheit behaftet, dass der Einfluss der thermischen Dissoziation auf den Schmelzpunkt nicht eindeutig berücksichtigt wurde. In einer kurzen Zusammenfassung von NISHIMURA[12] ist ein Diagramm abgebildet, nach dem bei 1825°C das Existenzgebiet von TiO_2 vollständig aufhört, und die Verbindung bei höherer Temperatur in gasförmigen Sauerstoff und eine an Sauerstoff wesentlich ärmere Schmelze zerfällt. Nach unseren Ergebnissen können die Phasenverhältnisse in diesem Gebiet aber nicht so beschaffen sein, wie NISHIMURA angibt.

SCHMELZAPPARATUR

Um im Gegensatz zu allen früher erwähnten Untersuchungen Titandioxyd unter willkürlich gegebenen, verschiedensten Sauerstoffdrucken erhitzen und schmelzen zu können, konstruierten wir eine Apparatur, die Temperaturen von mindestens 2000°C zu erzeugen und die Substanzprobe in die gewünschte Atmosphäre mit einer Variation des Sauerstoffdruckes zwischen Hochvakuum und 2 Atm zu bringen gestattete. Als Heizquelle diente uns dabei die mit einem Hohlspiegel fokussierte Sonnen strahlung (Sonnenofen[13–26]). Die technischen und berechneten Daten des rückseitig versilberten und sphärisch geschliffenen Glasspiegels sind aus folgender Zusammenfassung ersichtlich:

TABELLE 1

Spiegeldurchmesser	Durchmesser des Sonnenbildes	Brennweite	Numerische Öffnung	Energiedichte des Brennflecks	Theoret. Temperatur des Brennflecks	Gemessene Maximaltemperatur des Brennflecks
$D = 150$ cm	$d = 5{\cdot}97$ mm	$f = 64{\cdot}1$ cm	$\frac{D}{f} = 2{\cdot}34$	4263 w·cm^{-2}	4900°C	ca. 3000°C

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[13] *Oeuvres de Lavoisier recueillies par S. Ex. le Ministre de l'Instruction Publique*, Tomes I à IV. Paris, Imprimerie Impériale.
[14] A. MUCHOT, *C.R. Acad. Sci., Paris* **81**, 571 (1875).
[15] A. STOCK u. H. HEYNEMANN, *Ber. Dtsch. Chem. Ges.* **42**, 2863 (1909).
[16] W. M. CONN, *Trans. Electrochem. Soc.* **68**, 574 (1935).
[17] W. M. CONN, *Ceramic Digest* **1**, 349 (1951).
[18] F. TROMBE u. M. FOEX, *C. R. Acad. Sci., Paris* **223**, 317 (1946).
[19] F. TROMBE u. M. FOEX, *C. R. Acad. Sci., Paris* **225**, 1073 (1947).
[20] F. TROMBE u. M. FOEX, *Ann. Chim.* (12) **2**, 385 (1947).
[21] F. TROMBE u. M. FOEX, *C. R. Acad. Sci., Paris* **226**, 83 (1948).

Die Versuchsprobe mit ihrem Halter konnte durch ein Schlittensystem in drei Dimensionen verschoben und dadurch mit sehr grosser Genauigkeit an oder in den Brennfleck geführt werden. Durch diese Anordnung war es möglich, den Abstand der Probe zum Brennfleck exakt zu beherrschen und einen Probekörper langsam bis auf 3000°C zu erhitzen.

Damit die Probe unter verschiedenen Gasen und Gasdrucken erhitzt werden konnte, umgab man sie mit einem 4 *l*-Rundkolben aus Jenaerglas, so dass der Brennfleck genau im Zentrum des Kolbens lag.

DIE PRÄPARATE FÜR DIE SCHMELZVERSUCHE

TiO_2

Ein besonders reines Präparat von TiO_2 wurde dadurch gewonnen, dass man K_2TiF_6 mehrmals umkristallisierte.[27,28] Als Ausgangsmaterial hierfür diente ein von der Industrie vorgereinigtes Titandioxyd, dessen Reinheitsgrad sowohl chemisch als auch spektrographisch (Zeiss-Spektrograph Q 24) untersucht wurde. Die Substanz enthielt nur Spuren von Kupfer und Eisen. Ausserdem liess sich flammenspektroskopisch eine sehr geringe Spur Natrium nachweisen. Aus den Befunden konnte man für die Ausgangssubstanz einen Reinheitsgrad von etwa 99·8% TiO_2 abschätzen.

Ein Gewichtsteil dieses Oxyds wurde mit der doppelten Menge K_2CO_3 (p.a.) in einer Platinschale verschmolzen. Der erkaltete, feingepulverte Schmelzregulus wurde in der Platinschale mit wässriger verdünnter Flußsäure behandelt. Dabei schied sich K_2TiF_6 in Schuppen ab. Wir wählten einen kleinen Unterschuss an HF, damit die Säure vollständig verbraucht wurde und die Präparation anschliessend in Glasgefässen fortgesetzt werden konnte. Der K_2TiF_6-Brei wurde in etwa dem 5-fachen Volumen kochenden destillierten Wassers aufgelöst. Eine Verunreinigung durch SiO_2 trat hierbei nicht auf, wie die folgende chemische und spektrographische Prüfung ergab. Die filtrierte, heisse K_2TiF_6-Lösung wurde auf ein Drittel eingeengt und abgekühlt. Das sich abscheidende Hydrat kristallisierten wir noch drei Mal aus heissem Wasser um und rauchten es in einer Platinschale zwei Mal mit konz. H_2SO_4 ab. Die dadurch entstehende fluoridfreie Lösung von Titanylsulfat in Schwefelsäure unterwarfen wir der Hydrolyse mit verdünnter kieselsäurefreier wässriger Ammoniaklösung. Das ausgeflockte Titandioxydhydrat wurde abfiltriert, ausgewaschen, in warmer verdünnter H_2SO_4, gelöst und wieder mit Ammoniaklösung ausgefällt. Diesen Reinigungsprozess durch Umfällung wiederholten wir dreimal, spülten das Präparat nach der letzen Operation nochmals gründlich mit destilliertem Wasser aus, trockneten es bei 110°C und glühten es 3 Stunden bei 1000°C. Die anschliessende chemische, flammenspektroskopische und UV-spektrographische Untersuchung ergab höchste Reinheit des gewonnenen Titandioxyds.

Ti_2O_3

Reduziert man TiO_2 bei hohen Temperaturen mit Wasserstoff, dann erhält man nach Literaturangaben nur Oxyde der ungefähren Zusammensetzung $TiO_{1\cdot67}$ (Ti_3O_5).[29–34] Die in dieser Richtung sehr zahlreich beschriebenen Experimente ergaben fast übereinstimmend, dass durch Wasserstoffreduktion die Stufe Ti_2O_3 nicht zu erreichen war. Lediglich BELJAKOVA und MICHAILOW[35] glauben bei ihren Reduktionsversuchen bis 1500°C Ti_2O_3 erhalten und röntgenographisch nachgewiesen. zu haben. Wir wiederholten nochmals die Versuche, Titandioxyd durch Wasserstoff zu Ti_2O_3 abzubauen.

[22] F. TROMBE u. M. FOEX, *C.R. Acad. Sci., Paris* **228**, 986 (1949).
[23] F. TROMBE u. M. FOEX. *C.R. Acad. Sci., Paris* **228**, 1107 (1949).
[24] F. TROMBE u. M. FOEX, *C.R. Acad. Sci., Paris* **231**, 44 (1950).
[25] *Materials and Methods* **40**, 214 (1954).
[26] *Iron Age* **29**, 53 (1954).
[27] G. BRAUER, *Handb. Präp. Chem.* S 912. Enke-Verlag, Stuttgart (1954).
[28] L. VANINO, *Handb. Prap. Chem.* Band I, S. 498. Enke-Verlag, Stuttgart (1913).
[29] EBELMEN, *Ann. Chim. Phys.* **20**, 392 (1847).
[30] H. SAINTE-CLAIRE DEVILLE, *C.R. Acad. Sci., Paris* **82**, 1077 (1876).
[31] O. v. d. PFORDTEN, *Liebigs Ann.* **237**, 201 (1887).
[32] SOLTMANN, Thèse Berne (1903).
[33] M. BILLY, *Ann. Chim.* (9), **16**, 25 (1921).
[34] R. WYSS, *Ann. Chim.* (12), **3**, 215 (1948).
[35] I. BELJAKOWA, A. KOMAR u. W. MICHAILOW, *Metallurgist* **14**, 23 (1939).

Um einen möglichst hohen Reduktionsgrad zu erreichen, müssen hohe Temperaturen und lange Reaktionszeiten angewendet werden. Dabei stösst die Reinerhaltung der Wasserstoffatmosphäre auf gewisse Schwierigkeiten. Wie sich bei unseren Experimenten ergab, enthalten die gebräuchlichen keramischen Rohre, selbst reinste Sinterkorundrohre, stets Spuren von SiO_2. In der Wasserstoffatmosphäre bei hohen Temperaturen verwandelt sich SiO_2 in leichter flüchtiges SiO. Die Rohre werden dunkel gefärbt und undicht und lassen kleine Anteile von Luft eindringen. Diese Verunreinigung durch Luftsauerstoff führt zu einem Gasgleichgewicht, dessen Bodenkörper vermutlich der beobachteten Verbindung Ti_2O_5 entspricht. Wir glaubten, dass die erwähnten Misserfolge bei Versuchen, reines Ti_2O_3 durch Wasserstoffreduktion herzustellen, auf solche Ursachen zurückzuführen sind, und bemühten uns, die Störungen bei unseren Versuchen auszuschalten.

Unsere Reduktionsapparatur enthielt ein von Wasserstoff durchströmtes Sinterkorundrohr, in dem sich das Titandioxyd in einem Al_2O_3-Schiffchen befand. Dies Sinterkorundrohr wurde von einem Mantelrohr aus "Pythagorasmasse" umgeben, das durch gekühlte Gummistopfen vakuumdicht mit dem zentralen Rohr verbunden war und von Stickstoff durchströmt wurde. Wasserstoff und Stickstoff waren die reinsten, im Handel befindlichen Gase ("Elektrolytwasserstoff" und "Lampenstickstoff") und wurden in Türmen mit aktivem Kupfer von Sauerstoff, sowie über Kieselgel und Magnesiumperchlorat von Wasserspuren befreit. Das Rohrsystem mit dem darin befindlichen Schiffchen wurde durch einen elektrischen Röhrenofen mit Silitstäben als Heizelementen erhitzt.

Bei einer Reduktionstemperatur von 1430°C und einer Reduktionsdauer von 10 Stunden erhielten wir ein grauschwarzes, nicht ganz einheitliches Produkt, dessen Sauerstoffgehalt, durch quantitative Oxydation zu TiO_2 ermittelt, sich entsprechend der Formel $TiO_{1\cdot654}$ ergab. Nach einer Erhöhung der Reduktionsdauer auf 20 Stunden ergab sich ein Reduktionsgrad entsprechend $TiO_{1\cdot601}$. Nach einer Reduktionsdauer von 60 Stunden jedoch besass das Reduktionsprodukt die Zusammensetzung $TiO_{1\cdot460}$, und auch bei 70-stündiger Reduktion änderte sich nichts weiter an dieser Zusammensetzung. Die Analysenformel $TiO_{1\cdot46}$ unserer Präparate stimmt nun genau mit der Angabe von Ehrlich[36,37] für die untere Grenze der γ-Phase überein. Es erscheint sehr einleuchtend, dass die Wasserstoffreduktion gerade beim Erreichen dieser unteren Phasengrenze ihr Ende findet. Die vollständige Freiheit unserer Reduktionsprodukte von Aluminium und Silicium wurde UV-spektrographisch festgestellt.

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Oxydproben mit einer summarischen Zusammensetzung zwischen $TiO_{1\cdot46}$ und $TiO_{2\cdot00}$ stellten wir durch Mischung dieser beiden Grenzoxyde dar. Die Mischungen wurden später zu Presslingen verdichtet und homogenisierten sich von selbst im Verlauf der folgenden Erhitzungsprozesse.

AUSFÜHRUNG UND ERGEBNIS DER SCHMELZVERSUCHE

Die Oxydpresslinge

Alle Oxyde und Oxydmischungen wurden vor der Untersuchung zu zylindrischen Presslingen von 5·3 mm Durchmesser und etwa 45 mm Höhe geformt. Die Matrize der verwendeten Pressform war mit Glas ausgekleidet, um eine Verunreinigung der Proben mit Fremdmetall zu vermeiden. In den unteren Teil des Presslings wurde bereits während des Pressvorganges die Spitze eines dünnen Magnesiastäbchens eingefügt, welches bei den späteren Versuchen zur Halterung diente. (Vgl. Abb.2) Die so vorbereiteten Presslinge wurden noch im Vakuumexsiccator über Magnesiumperchlorat von den letzen Spuren Feuchtigkeit befreit.

Das Schmelzgefäss

Das Schmelzgerät (vgl. Abb. 3) enthielt, von einem Gummistopfen ausgehend, in dem bereits erwähnten Glaskolben die Untersuchungsprobe auf ihrem Magnesiastäbchen und daneben ein leeres Magnesiastäbchen als Hilfsgerät zum Aufsuchen des

[36] P. Ehrlich, *Z. Elektrochem.* **45**, 362 (1939).
[37] P. Ehrlich, *Z. Anorg. Chem.* **247**, 53 (1941).

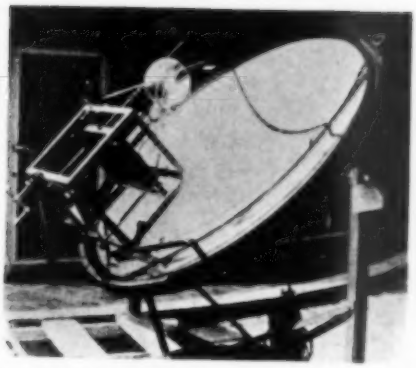

ABB. 1.—Sonnenofen mit Spiegel, Reaktionskolben und Bewegungs mechanismus des Kolbens.

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Brennflecks. Kolben und Gummistopfen wurden von einer Messingfassung getragen. Beide Magnesiumoxydstäbchen konnten gemeinsam durch eine Spindel, die vakuumdicht mit dem Kolbeninnern verbunden war, in der Höhe verstellt werden. Ausserdem führten zwei Bohrungen in das Kolbeninnere als Vakuumanschluss und zum Anschliessen einer Fussballgummiblase, die als Druckausgleich zum Konstanthalten des

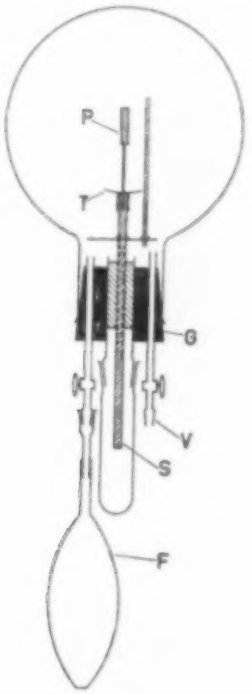

Abb. 3.—Schematische Darstellung des Schmelzgerätes
P—Probe, T—Schutzteller, G—Gummistopfen, V—Vakuumanschluss, S—Spindel F—Fussballblase.

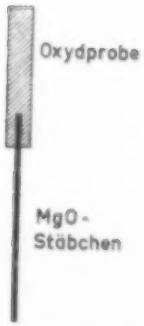

Abb. 2.—Oxydpressling.

Innendrucks diente. Der Gesamtgasdruck im Kolben wurde vor der Messung auf einen Wert eingestellt, welcher gleich der Grösse des äusseren Luftdruckes war, gleichgültig welches im Einzelfall der Partialdruck des Sauerstoffs in der Versuchsatmosphäre sein sollte. Die Gummiblase bewirkte, dass dieser Gesamtdruck unabhängig von Erwärmungen des Kolbens konstant blieb.

Gasfüllung des Schmelzgefässes

Es ist mit Hilfe des Sonnenofens und des beschriebenen Gerätes prinzipiell möglich, eine Substanz in beliebigen Gasatmosphären z.B. auch in reinem Sauerstoff und unter Gasdrucken von etwa 10^{-3} bis 2 Atm auf ungefähr 3000°C zu erhitzen. Die Lösung dieses apparativen Problems scheint anderswo bisher nicht so vollständig erreicht worden zu sein.

Zur Ermittlung des Sauerstoffgleichgewichtsdruckes von TiO_2 beim Schmelzpunktführten wir den Schmelzprozess an verschiedenen Proben von Titandioxyd unter verschiedenen Sauerstoffdrucken durch. Die genaue Einstellung der jeweils gewünschten O_2-Partialdrucke im Schmelzgefäss konnte mit Hilfe einer Gasdosierungsapparatur erreicht werden. Der Glaskolben mit der Titandioxydprobe wurde auf 10^{-4} Torr

evakuiert, mit gereinigtem und getrocknetem Sauerstoff gespült und erneut mit Sauerstoff bis zu einem bestimmten Partialdruck gefüllt. Ein angeschlossenes Quecksilbermanometer gestattete die Bestimmung dieses Druckes auf ein Torr genau. Zur Auffüllung auf Atmosphärendruck verwendeten wir gereinigtes und getrocknetes Argon.

Messung der Schmelztemperaturen von Titandioxyd unter Sauerstoffdrucken von 10^{-3} *Torr bis* 1·5 *Atm* O_2

Die bewegliche Aufhängung des Spiegels erlaubte wohl die grösste Schärfe des Fokus einzustellen, nicht aber seine Lage im Kolben zu ermitteln. Durch Ausnützung aller Verstellungsmöglichkeiten des Kolbens, einschliesslich einer Drehung um seine Längsachse tastete man mit dem MgO-Sucherstäbchen den Inneraum ab um die Position des Sonnenbildes genau zu erfahren, während sich die eigentliche Versuchsprobe noch abseits befand. Die Oxydprobe wurde nun von unten her dem Brennfleck vorsichtig genähert, so dass der obere Teil des Presslings langsam zu schmelzen begann. Durch weiteres Eindrehen der Probe in den Brennfleck war es leicht möglich, die flüssige Oxydkuppe zu vergrössern. Dies Verfahren bot die Möglichkeit, jede gewünschte Temperatur einzustellen und einzuhalten. Da die Temperatur des Glaskolbens relativ niedrig blieb, war eine Beobachtung des Schmelzvorganges aus etwa 12 cm Entfernung leicht möglich.

Zu Beginn der Verflüssigung waren im Oxydtropfen Schlieren sichtbar, die starken Wärmebewegungen unterworfen waren und nach einiger Zeit verschwanden. Dies deutete auf eine Selbsthomogenisierung der Schmelze hin. Die Vorrichtung musste stets senkrecht stehen, damit die Schmelze nicht abtropfte.

Zur Festlegung der Schmelztemperaturen eignete sich nur die strahlungspyrometrische Messung der Tropfenbildungstemperatur der Kuppe des Oxydstäbchens. Das Pyrometer (Pyropto, Firma Hartmann u. Braun, Frankfurt/M.) wurde zuvor gegen reinstes Al_2O_3, CaF_2, NiO und Cr_2O_3 geeicht, wobei die Eichsubstanzen unter Argon und denselben apparativen Bedingungen wie die zu untersuchenden Proben geschmolzen wurden. Um für die Strahlungsintensität der Substanz vergleichbare Werte zu erhalten, bezogen wir die für das hellgelbe TiO_2 gemessenen Werte auf die Eichwerte der weissen Verbindungen Al_2O_3 und CaF_2. Die reduzierten dunkelblauen Oxyde TiO_{2-x} dagegen verglichen wir mit den Werten der Eichsubstanzen Cr_2O_3 und NiO. Die Genauigkeit dieser Messmethode dürfte bei 2000°C etwa ±15°C betragen. Um die individuellen Beobachtungsfehler bei der pyrometrischen Temperaturmessung möglichst zu vermindern, wurden die Messungen von verschiedenen Personen durchgeführt. Bei den Temperaturangaben handelt es sich jeweils um das arithmetische Mittel von 6 Messungen.

Beim Schmelzen von Titandioxyd unter verschiedenen Sauerstoffdrucken ergaben sich die in Tabelle 2 zusammengefassten Beobachtungen.

Diese Beobachtungen erstrecken sich ausser auf die Schmelztemperaturen auch auf den Sauerstoffgehalt und die Farbe der Schmelzprodukte nach ihrer Abkühlung.

Die Prüfung der Abbauprodukte auf ihren Sauerstoffgehalt erfolgte durch nachträgliche Aufoxydation. Dafür trennte man die homogen geschmolzene Kuppe der abgekühlten Probe sorgfältig vom restlichen TiO_2-Stab, pulverisierte sie und glühte sie 24 Stunden bei 1300°C in reinem Sauerstoff. Dabei verlief die Oxydation zu TiO_2 quantitativ unter Farbänderung von schwarzblau nach hellgelb. Unser Befund steht im Gegensatz zu anderen Versuchsangaben,[5] nach denen die

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vollständige Oxydation der Abbauprodukte, freilich unter etwas anderen Bedingungen, nicht gelungen war.

Wie die Versuche aus Tabelle 2 zeigen, wird TiO_2 beim Schmelzen an Luft zu $TiO_{1.996}$ abgebaut. Diese Tatsache scheint bisher nicht hinreichend bekannt gewesen oder nicht beachtet worden zu sein. Beim Erhitzen von reinem Titandioxyd an Luft erreicht man also nicht einen wahren Schmelzpunkt, sondern einen Zersetzungspunkt.

TABELLE 2.—VERSUCHE UBER DAS SCHMELZEN VON TiO_2 IN VERSCHIEDENEN GASATMOSPHÄREN

Probe	Sauerstoff-Druck (Torr)	Argon-Druck (Torr)	Schmelzpunkt (°C)	Analyt. Zusammensetzung des erstarrten Schmelzproduktes	Entstandenes Sauerstoffdefizit x für TiO_{2-x} in Molen	Farbe d. erstarrten Schmelzproduktes n. OSTWALD[161]
1	10^{-3}	—	1795 ± 15	$TiO_{1.999}$	0·031	schwarzblau 15 pn
2	—	760	1800 ± 15	$TiO_{1.975}$	0·025	schwarzblau 15 pn
3	15	745	1820 ± 15	$TiO_{1.990}$	0·010	dunkelblau 14 pl
4	(159 Luft)	—	1830 ± 15	$TiO_{1.996}$	0·004	dunkelblau 14 pl
5	300	460	1840 ± 15	$TiO_{2.000}$	analyt. nicht mehr nachweisbar	dunkelgraublau 14 li
6	500	260	1860 ± 15	$TiO_{2.000}$	analyt. nicht mehr nachweisbar	hellblaugrau 15 lg
7	600	160	1870 ± 15	$TiO_{2.000}$	0	hellgelb 2 ea
8	760	—	1870 ± 15	$TiO_{2.000}$	0	hellgelb 2 ea
9	1140	—	1870 ± 15	$TiO_{2.000}$	0	hellgelb 2 ea

Schmilzt man die TiO_2-Probe unter 300 Torr Sauerstoffpartialdruck (Probe Nr. 5), dann ist wohl gewichtsanalytisch keine Sauerstoffabspaltung mehr nachweisbar; auf eine sehr geringe Abweichung von der ganzzahlig stöchiometrischen Zusammensetzung ist jedoch noch aus der Dunkelblaufärbung der Substanz zu schliessen. Erst bei 600 Torr Sauerstoffdruck bleibt das Titandioxyd während und nach dem Schmelzprozess hellgelb. Der Sauerstoffdruck des Dissoziations gleichgewichts beim Schmelzpunkt von TiO_2 liegt also etwa bei 600 Torr. Die unter diesen Bedingungen gemessene Schmelztemperatur hat einen Wert von 1870 ± 15°C und stellt den wahren Schmelzpunkt von unzersetztem TiO_2 dar.

Beim Schmelzen im Vakuum und in Argonatmosphäre findet naturgemäss auch

eine Sauerstoffabspaltung statt. Ihr Betrag ist für Vakuum und für Argon etwas verschieden (Versuchs-Nr. 1 und 2). Diese Differenz möchten wir dahingehend interpretieren, dass die Argonatmosphäre im Vergleich zum Vakuum eine diffusionshemmende Rolle spielt und eine Verzögerung der Sauerstoffabspaltung hervorruft. Bei der geringen Dauer eines einzelnen Versuchs von maximal 3 Minuten kann sich ein solcher Effekt sehr bemerkbar machen. Unter Umständen kann auch ein geringer Sauerstoffgehalt im Argon von Einfluss sein.

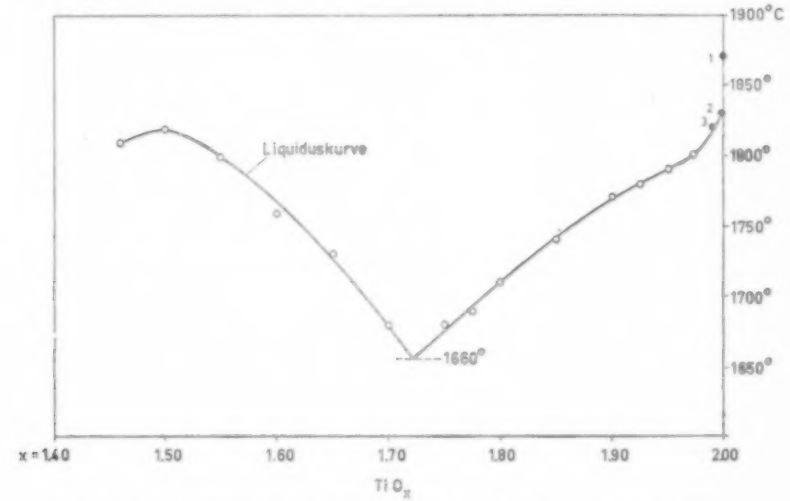

ABB. 4.—Schmelzdiagramm der Titanoxyde für den Bereich von $TiO_{1.46}$ bis TiO_2
●1 600 mm Hg Sauerstoffpartialdruck. ●2 150 mm Hg Sauerstoffpartialdruck.
●3 15 mm Hg Sauerstoffpartialdruck. ○ reine Argonatmosphäre.

Bei den Versuchen erwies sich, dass sorgfältig darauf geachtet werden musste, die Proben nicht zu weit in den Brennfleck zu drehen und dadurch zu überhitzen. Durch solche Überhitzungen würde nämlich die Sauerstoffabspaltung wesentlich erhöht und eine irreversible Inhomogenität verursacht werden.

Messung der Schmelztemperaturen von Oxyden $TiO_{1.460}$ *bis* TiO_2 *unter 760 Torr Argon*

Zur Aufstellung eines vollständigen Schmelzdiagrammes der sauerstoffreichen Titanoxyde wurden ausser den Untersuchungen des Dissoziationsgebietes von TiO_2 (TiO_2 bis $TiO_{1.975}$), deren Ergebnisse in Tabelle 2 enthalten sind, auch Schmelzpunktsbestimmungen der niederen Oxyde von $TiO_{1.46}$ bis $TiO_{1.975}$ ausgeführt. Da die untere Grenze des Dissoziationsgebietes von Titandioxyd bei $TiO_{1.975}$ liegt, konnten die Schmelzpunktsbestimmungen aller Oxyde mit niedrigerem Sauerstoffgehalt unter Argon ausgeführt werden, ohne dass die Substanzen dabei ihre Zusammensetzung veränderten. Die stöchiometrische Konstanz wurde jeweils nach dem Schmelzen durch Analyse (Verglühen bei 1300°C in reinem Sauerstoff) nachgewiesen. Die Ergebnisse der Messungen sind im Diagramm Abb. 4 dargestellt.

Nach diesen Befunden liegt der Schmelzpunkt von reinem Ti_2O_3 bei 1820 ± 15°C und nicht, wie von JUNKER[8] durch eine unsichere Extrapolation angegeben, bei 1900°C. Das von uns beobachtete Eutektikum bei der Zusammensetzung $TiO_{1.72}$

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(1655 ± 15°C) entspricht einem ähnlich liegenden eutektischen Punkt, den NISHIMURA[12] bei seinen Versuchen fand.

Es ist nicht ohne weiteres zu erkennen, wie diese Schmelzkurve mit den Existenzgebieten der in letzter Zeit aufgefundenen festen Phasen der Zusammensetzungen Ti_nO_{2n-1} ($n = 10$ bis 3)[38–47] vereinigt werden kann. Ein Widerspruch braucht nicht vorzuliegen, wenn die Zwischenoxyde nur bei tieferen Temperaturen als 1600°C stabil sind.

Die unter Argon geschmolzenen und anschliessend erstarrten niederen Oxyde sind ziemlich gleichförmig dunkelblau bis blauviolett gefärbt. Nach der OSTWALD'schen Farbskala[48] treten folgende Werte auf:

$TiO_{1.950}$ bis $TiO_{1.600}$: dunkelblau, 14 pl

$TiO_{1.550}$ bis $TiO_{1.460}$: blauviolett, 13 pl

Die thermische Dissoziation von TiO_2 *bei tieferen Temperaturen*

Wir untersuchten weiterhin die Sauerstoffgleichgewichtsdrucke von Titandioxyd zwischen 1000°C und 1300°C, um weitere Daten über die thermische Dissoziation des Oxyds zu gewinnen. Für das gleiche Temperaturintervall und Oxydproben im Bereich $TiO_{1.992}$ bis $TiO_{1.998}$ liegen bereits Messungen von ASSAYAG *et al.*[49] vor. Unsere eigenen experimentellen Befunde an $TiO_{2.00}$ als Ausgangsmaterial stehen mit diesen Messungen in gutem Einklang.

Wir massen die Zersetzungsdrucke von TiO_2 bei verschiedenen Temperaturen direkt manometrisch in einer Versuchsanordnung, deren Hauptteile ein vakuumdichtes elektrisch beheiztes Pythagorasrohr mit der Versuchsprobe und ein angeschlossenes U-förmiges Manometer mit Siliconölfüllung waren.

Das pulverförmige Titandioxyd wurde in einem röhrenförmigen Behälter in das Erhitzungsrohr eingebracht. Die Temperaturmessung erfolgte gleichzeitig durch ein Thermoelement und ein Strahlungspyrometer mit Anvisieren eines in der Pulverschicht ausgesparten Hohlraumes. Die Temperaturangaben beider Messmethoden stimmten sehr gut überein. Jeder Einzelversuch startete von einem Hochvakuum 10^{-5} Torr und führte bei konstanter Temperatur rasch zum Endwert der Druckeinstellung, die stets während einer Dauer von 2 Stunden überprüft wurde. Die Menge des Titandioxyds war so hoch bemessen, dass die Abspaltung von Sauerstoff zum Füllen des Apparatvolumens bis zum Gleichgewichtsgasdruck für die Zusammensetzung des Bodenkörpers nicht ins Gewicht fiel. Für die Druckzunahme durch die Gasabgabe der Apparatur beim Erhitzen wurde eine empirisch ermittelte Korrektur an den Messwerten für p_{O_2} angebracht.

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TABELLE 3

p_{O_2} (Torr)	log p	t(°C)	T(°K)	$1/T$
1·3	0·114	1050°	1323°	$7{\cdot}6 \times 10^{-4}$
2·0	0·301	1100°	1373°	$7{\cdot}3 \times 10^{-4}$
3·5	0·544	1150°	1423°	$7{\cdot}0 \times 10^{-4}$
6·3	0·800	1200°	1473°	$6{\cdot}8 \times 10^{-4}$
10·3	1·013	1250°	1523°	$6{\cdot}6 \times 10^{-4}$
12·9	1·111	1300°	1573°	$6{\cdot}4 \times 10^{-4}$

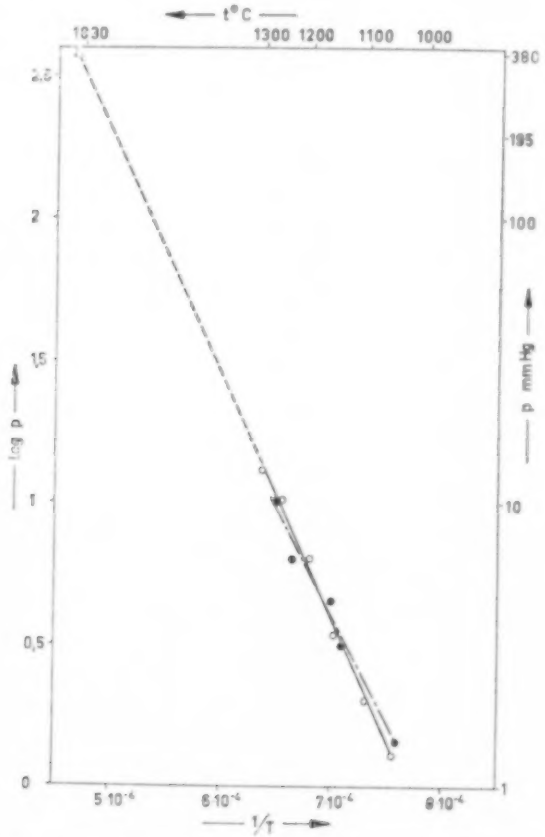

ABB. 5.—Temperaturabhängigkeit des Sauerstoffdissoziationsdrucks über Titanoxyden.
● O_2-Druck uber $TiO_{1\cdot906}$ (nach Assayag). ○ O_2-Druck über TiO_2 (eigene Messung).
▲ extrapolierter O_2-Druck beim Schmelzpunkt.

Tabelle 3 und Abbildung 5 geben die Messdaten und ihre graphische Einordnung im Diagramm log p vs. $1/T$ wieder.

Es ergibt sich in sehr befriedigender Weise und naher übereinstimmung mit den Zahlen von ASSAYAG[49] eine Gerade, deren Extrapolation zu höheren Temperaturen in unmittelbare Nähe des bei den Schmelzversuchen beobachteten Druckes von etwa 600 Torr bei 1870°C führt.

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ÜBER DIE OXYDE DES CERS—IV*

DIE SAUERSTOFFZERSETZUNGDRUCKE IM SYSTEM DER CEROXYDE

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Abstract—Systematic measurements of oxygen dissociation pressure in the system of the cerium oxides from CeO_2 to Ce_2O_3 are reported for the temperature range from 600 to 1050°C, using a dynamic method with given hydrogen–water-vapour mixtures. The oxygen dissociation pressures have values between 10^{-17} and 10^{-33} atm. From these results isotherms of the oxygen dissociation pressure are plotted as log p_{O_2} versus composition of the solid for 600, 700, 800, 900 and 1000°C. From the shape of these isothermes conclusions were made with respect to the phase relationships and the heats of formation of the system considered.

IN früheren Arbeiten[1,2,3] haben wir die Reduzierbarkeit von Cerdioxyd mittels strömenden Wasserstoffs sowie den Einfluss von Fremdoxydzusätzen auf die Geschwindigkeit dieser Reaktion untersucht. Aus diesen kinetischen Messungen konnten halbquantitative Aussagen erhalten werden, die gleichzeitig erlaubten, einige Unstimmigkeiten in den Aussagen älterer und neuerer Autoren über die Reduktion von CeO_2 zu deuten.† Zum Verständnis des Gesamtverhaltens der Ceroxyde fehlten jedoch bisher die fundamental wichtige Kenntnis ihrer Sauerstoffzersetzungsdrucke und damit sichere Unterlagen für ihre Bildungsenergien bei verschiedener Zusammensetzung.

In der Literatur finden sich lediglich bei SCHENK und ROTERS[4] Angaben über einige Gleichgewichtseinstellungen an Ceroxyden in einem CO_2–CO-Gasgemisch. Das Hauptziel dieser Arbeit lag allerdings im Nachweis der Beeinflussung des Redoxgleichgewichts durch zugesetzte Fremdoxyde. Dementsprechend sind auch die Angaben darin für reine Ceroxyde nur kurz und enthalten ausser der Feststellung, dass der Bodenkörper bei 700°C im Bereich $CeO_{1.98}$–$CeO_{1.96}$ und bei 900°C im Bereich $CeO_{1.96}$–$CeO_{1.89}$ einphasig ist, keine Berechnungen von Sauerstoffzersetzungsdrucken.

Über die systematische Messung der Sauerstoffzersetzungsdrucke im System der Ceroxyde CeO_2–Ce_2O_3 soll hier berichtet werden. Die gleichzeitig mit dieser Untersuchung durchgeführte röntgenographische Arbeit[6] diente zur Aufklärung der kristallchemischen Verhältnisse. Eine weitere röntgenographische Untersuchung durch BEVAN[5] zeigte zusätzlich, wie komplex das Phasenverhalten der Ceroxyde sein muss.

* Der Inhalt dieser Arbeit wurde in gekürzter Form auf dem 61. Annual Meeting of the American Ceramic Society in Chicago am 19. Mai 1959 von K. A. GINGERICH vorgetragen.

† Eine ausführliche Diskussion der hier nicht ausdrücklich zitierten bekannten Literatur über die Ceroxyde findet sich in der I. Mitteilung.

[1] I. Mitteilung: G. BRAUER u. U. HOLTSCHMIDT, *Z. Anorg. Chem.* **265**, 105 (1951).
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[6] G. BRAUER u. K. A. GINGERICH, *J. Inorg. Nucl. Chem.* **16**, 87 (1960).

Im Anschluss an die Messung der Sauerstoffzersetzungsdrucke führten wir ausserdem im Bereich $CeO_{2.00}$–$CeO_{1.78}$ eine röntgenographische Hochtemperaturuntersuchung[6] durch. Eine zusammenfassende Besprechung des Systems der Ceroxyde unter Berücksichtigung aller neueren Ergebnisse geben wir in Anschluss an diese letztere Untersuchung.

EXPERIMENTELLES

Untersuchungsverfahren. Die Sauerstoffzersetzungdrucke der Ceroxyde im experimentell zugänglichen Temperaturbereich sind für eine direkte Messung zu klein. Wir benutzten daher eine indirekte Methode und wählten die Gleichgewichtseinstellung der untersuchten Oxydpräparate mit gasförmigen Wasserstoff–Wasserdampf-Gemischen bekannter Zusammensetzung, für die über einen grossen Temperaturbereich aus bekannten Daten der zugehörige Sauerstoffpartialdruck berechnet werden kann. Die Gasgemische leiteten wir mit konstanter Geschwindigkeit über die Proben und verfolgten die Gleichgewichtseinstellung durch wiederholte Wägung des Oxydpräparats. Diese dynamische Gleichgewichtseinstellung verdiente den Vorzug, weil in den verwendeten Gasgemischen ein sehr einseitiges Verhältnis von Wasserstoff zu Wasserdampf vorlag. Ferner konnten auf diese Weise Störungen infolge Thermodiffusion besser als bei einer statischen Gleichgewichtseinstellung vermieden werden. Während einer Serie von Gleichgewichtsmessungen hielten wir den Wasserdampfpartialdruck konstant und untersuchten die Abhängigkeit zwischen Gleichgewichtszusammensetzung und Gleichgewichtstemperatur.

Wir konnten bei Temperaturen oberhalb 600°C die Gleichgewichtseinstellungen reversibel durchführen und sind der Ansicht, dass echte Gleichgewichtsbedingungen beobachtet wurden. Diese Feststellung findet eine Stütze in den Ergebnissen unserer röntgenographischen Hochtemperaturuntersuchung.[6]

Die aus den Gleichgewichtsdaten berechneten Sauerstoffpartialdrucke können als wahre Dampfdrucke der Ceroxyde bei den Untersuchungstemperaturen angesehen werden, da gemäss Brewer[7] bei diesen Oxyden die Bildung von flüchtigen Suboxyden erst bei sehr viel höheren Temperaturen beginnt. Ebenso traten unter unseren Versuchsbedingungen auch keine flüchtigen Hydroxyde auf, wie dies für Berylliumoxyd[8] und Zinkoxyd[9] bekannt ist.

Apparatur. Die für die Untersuchung verwendete Apparatur musste die völlige Befreiung des Ausgangswasserstoffs von Sauerstoff und Wasserspuren gestatten und es ermöglichen, diesem Wasserstoff einen Zusatz von Wasserdampf von wohldefiniertem, auch über längere Zeit konstant zu haltenden Partialdruck beizumischen. Ferner mussten die Präparate ihrer Pyrophorität wegen unter Luftabschluss hantiert werden können. Abbildung 1 zeigt schematisch die Apparatur.

Zur Entfernung von Sauerstoff und Wasser passierte der aus einer Stahlflasche entnommene vorgereinigte Elektrolytwasserstoff nacheinander einen mit Schwefelsäure beschickten Blasenzähler, eine auf etwa 180°C geheitzte, mit aktiviertem Kupfer beschickte Säule, ein Rohr mit Kieselgel und ein U-Rohr mit Phosphorpentoxyd. Darauf folgte, durch einen gasdichten Tombakschlauch verbunden, ein 4 Liter-Kolben k mit wässriger Schwefelsäure oder Rohrzuckerlösung in einem auf 0·1°C genau regulierten Thermostaten. In diese Flüssigkeit wurde der Wasserstoff unter Überdruck von etwa 150 mm Hg durch eine G 3-Fritte in Form feiner Gasbläschen eingespresst, die sich beim Hochperlen mit einem bestimmten Wasserdampfdruck beluden. Ein System von Hähnen gestattete es den Kolben zu umgehen und bei Bedarf auch den trockenen Wasserstoff zu entnehmen. Es folgte das ebenfalls mit einem Tombakschlauch verbundene Reaktionsrohr aus Quarzglas mit dem Wägerohr w. Ein Blasenzähler mit konz. Schwefelsäure bildete den Abschluss. Während sämtlicher Versuchsreihen wurde eine ziemlich konstante Strömungsgeschwindigkeit von ca. 2·5 bis 3 Litern pro Stunde eingehalten.

Die Handhabungen beim Wägen der Ceroxydpräparate, die sich in einem Korundschiffchen befanden, erfolgten in ähnlicher Weise, wie bei unseren früheren Untersuchungen.[1] Eine kleine Verbesserung der früher beschriebenen Apparatur war dahingehend angebracht worden, dass das Reaktionsrohr nicht mehr mit aufgekitteten Schliffen versehen war, sondern, wie aus der Abbildung 1

[7] L. Brewer, *Chem. Rev.* **52**, 1 (1953).
[8] J. I. Grossweiner u. R. L. Seifert, *J. Amer. Chem. Soc.* **74**, 2701 (1952).
[9] O. Glemser, H. G. Völz u. B. Meyer, *Z. Anorg. Chem.* **292**, 311 (1957).

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hervorgeht, aus einem Stück bestand und in der Mitte eine Verjüngung hatte. Diese war so angebracht, dass beim Wiedereinziehen des Schiffchens dieses genau in der Ofenmitte stehen blieb. Bei jeder Unterbrechung der Gleichgewichtseinstellung zwecks Wägung wurde das heisse Schiffchen mit dem Oxydpräparat in eine wassergekühlte Zone *a* des Reaktionsrohres hineingestossen und so aus dem Gleichgewichtszustand abgeschreckt. Es war nötig, dabei das Wasserstoff–Wasserdampfgemisch durch gereinigten Stickstoff (Anschluss t) zu verdrängen. Beide Massnahmen verhinderten, dass beim Abkühlen eine Aufoxydation stattfand. Beim Wiedereinführen des gewogenen Präparates in den Ofen zur Fortsetzung der Messreihe wurde Vorsorge getroffen, dass das Präparat möglichst sofort wieder den gewünschten Gleichgewichtsbedingungen ausgesetzt war. Dazu wurde der Ofen

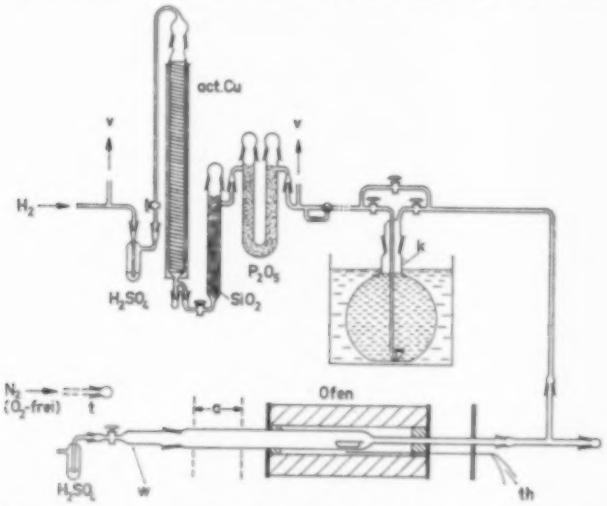

Abb. 1.—Apparatur zur Erhitzung von Ceroxyden im Wasserstoff-Wasserdampf-Strom. (v Quecksilberventile, k Kolben mit Schwefelsäure oder Zuckerlösung, th Thermoelement, w Wägerohr, a gekühlte Zone, t Anschluss für gereinigten Stickstoff).

zuvor auf eine empirisch ermittelte Übertemperatur geheizt, die so gewählt war (etwa 30°C über der Gleichgewichtstemperatur bei 600°C und 70 bis 80° bei 1000°C), dass aus dem Temperaturausgleich zwischen Ofen und kaltem Präparat sofort die gewünschte Gleichgewichtstemperatur resultierte.

Die Reinigung des Stickstoffs erfolgte in einer besonderen Anlage in der gleichen Weise wie die des Wasserstoffs.

Die Präparate wurden durch einen Röhrenofen mit Megapyrdrahtwicklung beheizt, dessen Temperatur im Bereich von 500 bis 1200°C genau geregelt werden konnte. Die Temperaturverteilung längs des Korundschiffchens mit dem Ceroxyd-Präparat war auf $\pm 2{\cdot}5$°C konstant. Die Temperaturmessung erfolgte mittels eines Pt/Pt-Rh Thermoelements th. Thermoelement und Temperaturanzeigeinstrument waren vorher mit dem Schmelzpunkt des Silbers (960°C) geprüft worden.

Bestimmung der Wasserdampfdrucke. Bei einer Bestimmung des Wasserdampfdrucks wurde anstelle des Wägerohres ein Verjüngungsstück in das Quarzrohr eingesetzt und daran ein mit Phosphorpentoxyd gefülltes U-Rohr angeschlossen. Die gebundene Wassermenge wurde durch Wägung aus der Gewichtsdifferenz des U-Rohres vor und nach einer bestimmten Versuchszeit ermittelt. Das Wasserstoffvolumen, das während dieser Versuchszeit die Apparatur durchströmt hatte, wurde mittels eines Gasometers unter Berücksichtigung des herrschenden Luftdrucks bestimmt.

In Vorversuchen stellten wir fest, dass Schwefelsäuren aus dem Konzentrationsbereich zwischen 80 und 68 Gewichtsprozent Wasserdampfdrucke besitzen, die günstig für die Einstellung von Reduktionsgleichgewichten in weiten Bereichen des Systems CeO_2–Ce_2O_3 sind. Die grosse Menge der Schwefelsäure (jeweils 6·5 bis 7 kg) gewährleistete eine Konstanz des Dampfdrucks über lange Versuchszeiten. Diese Konstanz haben wir am Ende einer jeden Serie von Gleichgewichtseinstellungen analytisch überprüft und bestätigt. Die Wasserdampfpartialdrucke, die sich bei unserer Versuchsführung bei den verschiedenen Säurekonzentrationen einstellten, waren 0·088, 0·28, 0·58, 0·86 und 0·93 mm Hg.

Zur Einstellung eines Wasserdampfpartialdruckes in der Nähe des Sättigungsdruckes des Wassers bei Raumtemperatur benutzten wir eine 55proz. (etwa 2 molare) Rohrzuckerlösung. Die Viskosität dieser Lösung war ähnlich wie bei den verwendeten Schwefelsäuren gross genug, um ein Verspritzen der Flüssigkeit in Apparateteile ausserhalb des Thermostaten zu vermeiden. Gleichzeitig änderte sich die Molarität dieser Lösung bei der Entnahme von etwa 60 cm^3 Wasser während der Messreihe nur so geringfügig, dass die damit verbundene Dampfdruckerhöhung vernachlässigt werden durfte. Mehrfaches Überprüfen ergab, dass der Dampfdruck innerhalb der Messgenauigkeit konstant 15·9 mm Hg blieb.

Ausgangspräparate. Als Ausgangsmaterial für unsere Untersuchung stand ein 99·8proz. Ceroxyd zur Verfügung. Dies wurde, ähnlich wie wir es in einer früheren Mitteilung[11] beschrieben, einer besonderen Reinigung unter Verwendung der von BOCK[10] angegebenen Methoden unterworfen. Die Farbe des auf diese Weise gereinigten Cerdioxyds ist beinahe rein weiss mit einem ganz schwach gelblichen Farbton. Hier sei noch eine Bemerkung über die Farbe von Ce_2O_3 eingefügt: Reinstes Ce_2O_3 ist goldgelb ohne jenen olivfarbenen oder grünlichen Stich, mit dem es sonst beschrieben wird. Präparate, die die unreinen Farbtöne zeigen, sind bereits schwach oxydiert.

Einstellung der Reduktionsgleichgewichte. Zur experimentellen Einstellung eines Gleichgewichts wurde eine eingewogene Menge CeO_2 dem strömenden Wasserstoff–Wasserdampf-Gemisch bekannter Zusammensetzung bei einer bestimmten Temperatur ausgesetzt. Die Temperatur war so gewählt, dass der Sauerstoffzersetzungsdruck des Oxydpräparats über dem Sauerstoffpartialdruck der Gasphase lag. Bei einem beliebigen Reduktionsgrad wurde die Reduktion abgebrochen und die Temperatur soweit erniedrigt, bis der Zersetzungsdruck unter dem Sauerstoffdruck der Gasphase lag, so dass also wieder eine geringe Oxydation eintrat, feststellbar am Gewicht des Präparats. Durch weiteres Eingabeln erhielt man schliesslich die Temperatur des Gleichgewichts, bei der der Zersetzungsdruck und Partialdruck in der Gasphase identisch sind, die Probe also gewichtskonstant blieb. Beispielsweise fanden wir auf diese Art für die Messreihe bei 0·088 mm Hg Wasserdampfdruck, dass für den Bereich $CeO_{1\cdot67}$–$CeO_{1\cdot50}$ eine Gleichgewichtstemperatur von 860 °C existiert, die unabhängig von der Bodenkörperzusammensetzung ist. Oxydpräparate $CeO_{1\cdot655}$, $CeO_{1\cdot613}$, $CeO_{1\cdot575}$, $CeO_{1\cdot56}$, $CeO_{1\cdot53}$ und $CeO_{1\cdot50}$ blieben bei 24-stündiger Exposition gewichtskonstant. Ein Erhitzen von $CeO_{1\cdot50}$ bei 850 °C hatte Oxydation zu $CeO_{1\cdot510}$ zur Folge. Die sauerstoffreiche Grenze des Bereichs wurde dadurch ermittelt, dass reines CeO_2 der Temperatur 860 °C ausgesetzt wurde; nach acht Tagen war Gewichtskonstanz bei einer Zusammensetzung von $CeO_{1\cdot67}$ oder $CeO_{1\cdot669}$ erreicht. Ausserdem wurde ein Präparat $CeO_{1\cdot670}$ je 24 Stunden einer etwas niedrigeren (850 °C) und einer etwas höheren (870 °C) Temperatur ausgesetzt. Im ersten Falle trat Oxydation zu $CeO_{1\cdot670}$ ein, im zweiten Falle Reduktion zu $CeO_{1\cdot656}$. In der weiteren Verfolgung dieser Messreihe bei 0·088 mm Hg Wasserdampfdruck wurde nun von CeO_2 ausgehend die Temperatur gesenkt. Bei 800, 700 und 600 °C fand Reduktion statt, bis sich jeweils eine bestimmte Zusammensetzung, nämlich $CeO_{1\cdot732}$, $CeO_{1\cdot795}$ und $CeO_{1\cdot869}$ einstellte und bei weiterer Versuchsdauer konstant blieb. Geringe Erniedrigungen der Temperatur unter die drei genannten, speziellen Werte hatte wieder eine Oxydation zur Folge, geringe Erhöhung der Temperatur bewirkte wieder eine Reduktion. Innerhalb dieses Mittelbereichs $CeO_{1\cdot86}$–$CeO_{1\cdot67}$ bestand also eine Abhängigkeit der Gleichgewichtstemperatur von der Bodenkörperzusammensetzung.

In gleicher Weise wurde bei den Wasserdampfpartialdrucken 0·28 und 0·93 mm Hg gefunden, dass Bodenkörperzusammensetzung und Gleichgewichtstemperatur im Zwischengebiet $CeO_{1\cdot85}$–$CeO_{1\cdot67}$ stark voneinander abhängig, im Gebiet $CeO_{1\cdot67}$–$CeO_{1\cdot50}$ dagegen voneinander unabhängig sind. Bei der Messreihe mit 0·58 mm Hg Wasserdampfpartialdruck wurde das Verfahren zur Bestimmung der Gleichgewichtstemperatur für den Bereich $CeO_{1\cdot67}$–$CeO_{1\cdot50}$ dahingehend abgekürzt, dass nur diejenige Temperatur aufgesucht wurde, bei der Cerdioxyd zu $CeO_{1\cdot670}$ reduziert wurde. Die Messwerte für alle diese Gleichgewichte sind in Tabelle 1 aufgeführt.

Bei den Wasserdampfpartialdrucken 0·93, 0·28 und 0·088 mm Hg wurden auch Messungen im Bereich $CeO_{2\cdot00}$–$CeO_{1\cdot85}$ vorgenommen. Bei diesen Bedingungen liegen die Gleichgewichtstemperaturen relativ niedrig. Gewichtsverschiebungen in der Nähe der Gleichgewichtslage erfolgen nur sehr langsam, und die definitive Einstellung kann erst in sehr langen Zeiten erreicht werden. Beim Wasserdampfdruck 0·088 mm Hg lagen die Gleichgewichtstemperaturen für den Bereich $CeO_{2\cdot00}$–$CeO_{1\cdot85}$ schätzungsweise zwischen 500 und 550 °C, und die Gleichgewichtseinstellungen liessen sich innerhalb von zwei bis drei Wochen überhaupt nicht mehr durchführen. Es wurden zwar zu Beginn

[10] R. BOCK, *Z. angew. Chem.* **62**, 375 (1950).

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der Untersuchung einige solche Messungen ausgeführt; deren Ergebnisse liessen sich aber nicht mit den bei 0·86 mm Hg Wasserdampfpartialdruck erhaltenen vereinbaren, entsprachen offenbar keinen echten Gleichgewichtsbedingungen und wurden deshalb nicht berücksichtigt.

Bei der Reihe mit 0·86 mm Hg Wasserdampfdruck zeigte sich für den Bereich $CeO_{2\cdot00}$–$CeO_{1\cdot85}$, dass einer sehr geringfügigen Änderung der Temperatur eine sehr grosse Änderung in der Gleichgewichtszusammensetzung entspricht. Eine genaue Konstanthaltung der Temperatur längs des ganzen Oxydpräparats war daher wesentlich. Wir bauten für diesen Zweck einen Röhrenofen von ca. 36 cm Länge, bei welchem sich der Abstand der einzelnen Heizleiterspiralen von der Ofenmitte ausgehend nach den Ofenenden zu stetig verringerte. Dadurch wurde in der Ofenmitte eine besonders gleichförmige Zone erhalten, in welcher beispielsweise eine Temperatur von 650°C auf 7 cm Länge mit ±0·5°C konstant war. Auf diese Weise waren die maximal möglichen zeitlichen Temperaturschwankungen auf der ganzen Länge des Präparats während einer beliebig langen Versuchsdauer auf weniger als ±1·5°C herabgemindert.

Im Bereich $CeO_{1\cdot95}$–$CeO_{1\cdot88}$ wurden keine Gleichgewichte festgelegt. Bei 615°C trat langsame Reduktion von CeO_2 bis zu einer Zusammensetzung $CeO_{1\cdot88}$ ein, während ein reduziertes Präparat bei 600°C zu $CeO_{1\cdot98}$ oxydiert wurde. In diesem Bereich ist die Gleichgewichtstemperatur offensichtlich von der Bodenkörperzusammensetzung unabhängig und lässt sich auf 610°C schätzen. Im Bereich $CeO_{1\cdot88}$–$CeO_{1\cdot85}$ dagegen konnte für eine bestimmte Temperatur reversibel eine bestimmte Zusammensetzung eingestellt werden, obgleich die Abhängigkeit der Temperatur von der Zusammensetzung um ein Vielfaches geringer ist als im Bereich $CeO_{1\cdot95}$–$CeO_{1\cdot87}$.

Der Bereich $CeO_{2\cdot00}$–$CeO_{1\cdot90}$ wurde zusätzlich bei einem Wasserdampfpartialdruck von 15·9 mm Hg untersucht. Die entsprechenden Gleichgewichtstemperaturen liegen hier hoch genug, um eine Gleichgewichtseinstellung schon in wenigen Tagen zu ermöglichen. Wir fanden, dass für den ganzen Bereich eine Abhängigkeit zwischen Temperatur und Zusammensetzung besteht.

Bei dieser Messreihe wurden die früher beschriebenen experimentellen Massnahmen in einigen Punkten ergänzt: Die Präparate wurden zur Wägung nicht in Stickstoff, sondern in trockenem Wasserstoff abgeschreckt, um Störungen durch den hohen Wasserdampfgehalt des Reaktionsgases beim Abkühlen zu vermeiden und dann erst unter Stickstoff gewogen. Wir prüften, dass eine zusätzliche Reduktion durch den reinen Wasserstoff vernachlässigt werden konnte. Weiterhin wurde bei dieser Messreihe darauf geachtet, ob sich während der Versuche flüchtige Verbindungen bildeten. Dazu wurde am Ende jeder Versuchsserie das Oxydpräparat zu CeO_2 verglüht. Es ergab sich, dass selbst bei einer Versuchsserie von zwei Wochen Dauer die eingesetzte Cerdioxydmenge unverändert geblieben war.

ERGEBNISSE UND DISKUSSION

Sauerstoffdrucke. Die Ergebnisse der Gleichgewichtsmessungen sind in Tabelle 1 zusammengestellt. In ihr sind die verschiedenen Messreihen nach steigendem Wasserdampfpartialdruck angeordnet, die Gleichgewichtsdaten innerhalb einer Messreihe nach steigender Temperatur. Die Zusammensetzung der Bodenkörper wird durch eine summarische Formel CeO_n (Bruttoformel) wiedergegeben. Der mittlere Fehler der Bestimmung der Zusammensetzung ist mit ±0·002 am Wert des Koeffizienten n zu veranschlagen. Die Sauerstoffpartialdrucke der Gasphase wurden gemäss der Beziehung

$$\log K_p = \log\left[\frac{p_{H_2} \times p_{O_2}^{\frac{1}{2}}}{p_{H_2O}}\right]$$

berechnet. Die Werte von log K_p für die einzelnen Temperaturen wurden den Tabellen von ZEISE[11] entnommen. Die log K_p-Werte für Temperaturen unterhalb 1000°K sind in den Tabellen nicht enthalten und mussten durch Extrapolation bestimmt werden. Da unsere Messungen unter Gleichgewichtsbedingungen ausgeführt wurden, sind die so berechneten Sauerstoffpartialdrucke der Gasphase identisch mit den Sauerstoffzersetzungsdrucken der betreffenden Ceroxyde

[11] H. ZEISE, *Z. Elektrochem.* **43**, 704 (1937).

Tabelle 1.—Reduktionsgleichgewichte und sauerstoffzersetzungsdrucke der ceroxyde

Versuch Nr.	p_{H_2O} (mm Hg)	Gleichgewichtstemp. (°C)	Zusammensetzung im Gleichgew. (Bruttoformel)	Richtung der Gleichgewichtseinstellung	p_{O_2} (Atm)
1†	0·088	540	$CeO_{1.850}$	R u. O‡	$1{\cdot}4 \times 10^{-24}$
2		600	$CeO_{1.830}$	R u. O	$2{\cdot}0 \times 10^{-21}$
3		700	$CeO_{1.797}$	R u. O	$2{\cdot}2 \times 10^{-18}$
4		800	$CeO_{1.742}$	R u. O	$6{\cdot}7 \times 10^{-17}$
5–11		860	$CeO_{1.67-1.50}$	—	$1{\cdot}3 \times 10^{-15}$
12	0·28	585	$CeO_{1.850}$	R u. O	$6{\cdot}4 \times 10^{-22}$
13		600	$CeO_{1.845}$	R u. O	$2{\cdot}0 \times 10^{-21}$
14		700	$CeO_{1.815}$	R u. O	$1{\cdot}9 \times 10^{-18}$
15		800	$CeO_{1.775}$	R u. O	$6{\cdot}7 \times 10^{-16}$
16		900	$CeO_{1.723}$	R u. O	$8{\cdot}1 \times 10^{-14}$
17–22		950	$CeO_{1.67-1.50}$	—	$6{\cdot}4 \times 10^{-13}$
23	0·58	625	$CeO_{1.850}$	O	$6{\cdot}2 \times 10^{-20}$
24		700	$CeO_{1.839}$	R	$9{\cdot}8 \times 10^{-19}$
25		800	$CeO_{1.797}$	R	$2{\cdot}9 \times 10^{-15}$
26		900	$CeO_{1.753}$	R	$3{\cdot}5 \times 10^{-13}$
27		1000	$CeO_{1.670}$	R	$1{\cdot}8 \times 10^{-11}$
28	0·86	600	$CeO_{1.888}$	O	$2{\cdot}00 \times 10^{-20}$
29		616	$CeO_{1.872}$	R u. O	$7{\cdot}60 \times 10^{-20}$
30		620	$CeO_{1.860}$	R	$9{\cdot}55 \times 10^{-20}$
31		623	$CeO_{1.864}$	R u. O	$1{\cdot}20 \times 10^{-19}$
32†		640	$CeO_{1.850}$	O	$5{\cdot}01 \times 10^{-19}$
33	0·93	655	$CeO_{1.850}$	R u. O	$1{\cdot}3 \times 10^{-18}$
34		700	$CeO_{1.838}$	R u. O	$2{\cdot}5 \times 10^{-17}$
35		800	$CeO_{1.813}$	R u. O	$7{\cdot}6 \times 10^{-15}$
36		900	$CeO_{1.778}$	R u. O	$9{\cdot}1 \times 10^{-13}$
37		1000	$CeO_{1.730}$	R u. O	$4{\cdot}5 \times 10^{-11}$
38–42		1045	$CeO_{1.67-1.50}$	—	$2{\cdot}5 \times 10^{-10}$
43	15·9	600	$CeO_{1.998}$	R	$2{\cdot}19 \times 10^{-17}$
44		650	$CeO_{1.992}$	R	$3{\cdot}02 \times 10^{-16}$
45		680	$CeO_{1.989}$	O	$2{\cdot}09 \times 10^{-15}$
46		700	$CeO_{1.986}$	O	$7{\cdot}20 \times 10^{-15}$
47		720	$CeO_{1.969}$	O	$2{\cdot}40 \times 10^{-14}$
48		750	$CeO_{1.935}$	R u. O	$1{\cdot}51 \times 10^{-13}$
49		760	$CeO_{1.932}$	R u. O	$2{\cdot}52 \times 10^{-13}$
50		780	$CeO_{1.907}$	R	$8{\cdot}32 \times 10^{-13}$
51		795	$CeO_{1.899}$	R u. O	$1{\cdot}82 \times 10^{-12}$
52		805	$CeO_{1.889}$	R u. O	$3{\cdot}02 \times 10^{-12}$
53		825	$CeO_{1.882}$	R u. O	$8{\cdot}71 \times 10^{-12}$
54		835	$CeO_{1.868}$	R u. O	$1{\cdot}26 \times 10^{-11}$
55†		870	$CeO_{1.827}$	R	$4{\cdot}37 \times 10^{-11}$
56†		940	$CeO_{1.82}$	R	$1{\cdot}45 \times 10^{-10}$
57		1050	$CeO_{1.790}$	R u. O	$9{\cdot}55 \times 10^{-10}$

† Diese Messungen sind infolge von Besonderheiten der Versuchsführung weniger sicher als die übrigen.
‡ O bedeutet Gleichgewichtseinstellung durch Oxydation, R durch Reduktion.

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In Abbildung 2 sind als unmittelbare Versuchsergebnisse die Gleichgewichtstemperaturen in Abhängigkeit von der Bodenkörperzusammensetzung aufgetragen, geordnet nach den verschiedenen konstanten Wasserdampfdrucken. Die daraus abgeleitete Abhängigkeit des Sauerstoffdrucks von der Bodenkörperzusammensetzung

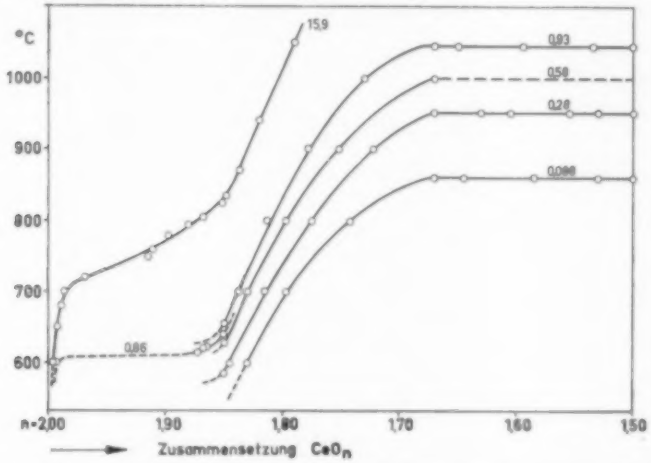

Abb. 2.—Gleichgewichtstemperaturen und Bodenkörperzusammensetzungen bei der Umsetzung von Ceroxyden mit Wasserstoff-Wasserdampf-Gemischen. (Die angeschriebenen Parameter 15·9, 0·93, 0·58, 0·28 und 0·088 sind die Wasserdampfdrucke in mm Hg für die einzelnen Messreihen.)

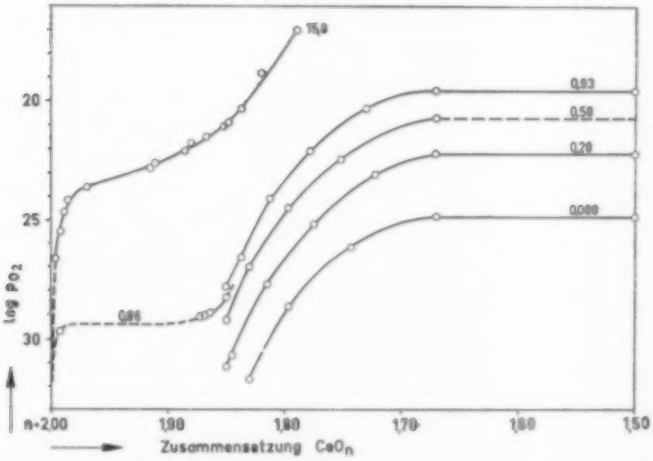

Abb. 3.—Abhängigkeit des Sauerstoffzersetzungsdruckes von der Bodenkörperzusammensetzung bei Ceroxyden. (Die angeschriebenen Parameter 15·9, 0·93, 0·58, 0·28 und 0·088 sind die Wasserdampfdrucke in mm Hg für die einzelnen Messreihen.)

ist in Abbildung 3 dargestellt. Längs der Kurven dieser Abbildung variiert die Temperatur. Durch Herausgreifen geeigneter Kurvenpunkte gelangt man zu der üblichen Darstellung mit Isothermen. So ist in der Abbildung 4 die Abhängigkeit der log p_{O_2}-Werte von der Bodenkörperzusammensetzung durch Isothermen für 600, 700, 800, 900 und 1000°C dargestellt. Die log p_{O_2}-Werte wurden direkt aus

Versuchsdaten berechnet (Tabelle 1) oder graphisch ermittelt. Zur graphischen Ermittlung wurden für eine bestimmte Zusammensetzung im Bodenkörper die log p_{O_2}-Werte in Abhängigkeit von der reziproken absoluten Temperatur $1/T$ aufgetragen. Man erhält so Geraden, aus denen sich die Sauerstoffzersetzungsdrucke

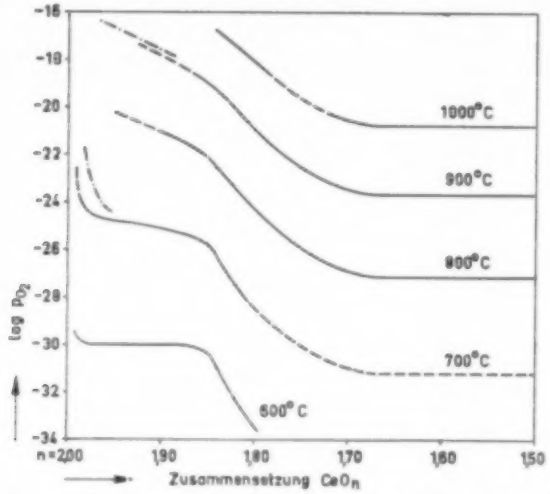

ABB. 4.—Isothermen des Sauerstoffzersetzungdruckes von Ceroxyden.

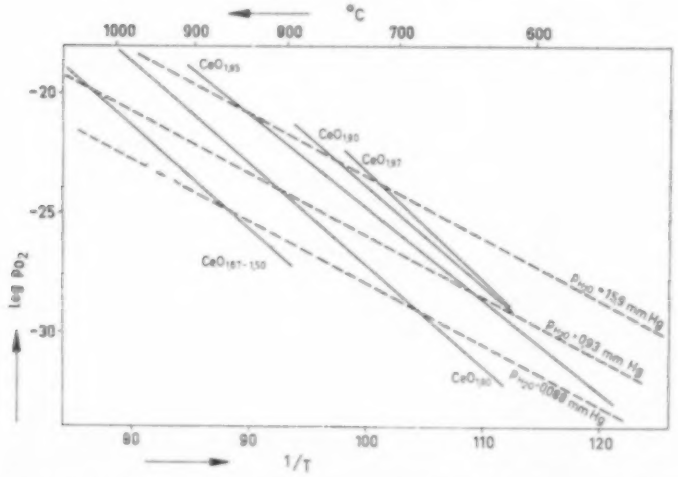

ABB. 5.—Abhängigkeit von Sauerstoffzersetzungsdruck und Temperatur bei Ceroxyden.

für beliebige andere Temperaturen ableiten lassen (siehe Abb. 5). Diejenigen Werte solcher Art, die durch Extrapolation über den Bereich der Messdaten hinaus ermittelt wurden, liegen in Abbildung 4 auf gestrichelten Linien. Schliesslich sind in dieser Abbildung auch noch log p_{O_2}-Werte für 700 und 900°C eingezeichnet, die wir aus den Analysenangaben von R. SCHENK und H. ROTERS berechnet haben.

Phasenverhältnisse. Aus den Isothermen der Abbildung 4 lassen sich nun wesentliche Schlüsse auf die Phasenverhältnisse des ganzen Oxydsystems ziehen. Der

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horizontale Verlauf sämtlicher Isothermen im Bereich $CeO_{1.50}$ bis $CeO_{1.67}$ beweist, dass in diesem Bereich der Bodenkörper aus zwei koexistierenden Phasen besteht. Die eine davon ist zweifellos das hexagonale Oxyd Ce_2O_3, die andere entspricht der Grenzzusammensetzung $CeO_{1.67}$ und ist identisch mit der früher[2] als Zwischenphase bezeichneten Verbindung mit fluoritähnlicher Kristallstruktur. Von dieser Zusammensetzung aus erstreckt sich nach höherem Sauerstoffgehalt hin ein Einphasengebiet bis etwa $CeO_{1.85}$, bei dem die Isothermen stetig ansteigen. Im Gebiet bei $CeO_{1.85}$ ändern die Isothermen bei tieferen Temperaturen mehr oder weniger stark ihre Richtung. Die Kurve bei 600°C verläuft zwischen $CeO_{1.88}$ und $CeO_{1.98}$ horizontal,

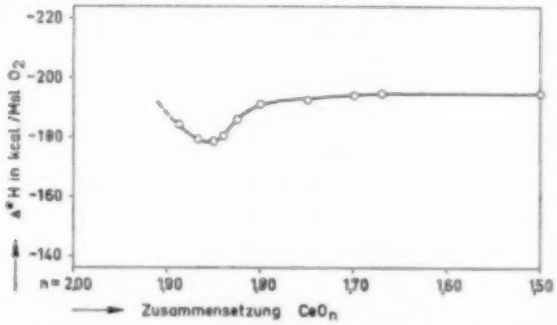

Abb. 6.—Partielle molare Bildungsenthalpien von Ceroxyden.

ein Zeichen, dass wieder ein Zweiphasengebiet mit Cerdioxyd und einem etwas sauerstoffärmeren Oxyd vorliegt. Die Kurven bei 700 und 800°C haben keine Horizontalen, sondern nur etwas flacher verlaufende Teile. Nach dem Gibbs'schen Phasengesetz kann deshalb in diesem Bereich nur eine Phase existieren. Der besondere Verlauf der Isothermen deutet aber auf starke Störungszustände dieser Phase hin, die mit steigender Temperatur verschwinden. Mit den früheren Röntgenbefunden[2] stand diese Beobachtung nicht in Einklang. Wir konnten aber neuerdings die Erklärung durch Röntgenaufnahmen an solchen Präparaten bei höherer Temperatur finden, bei denen wir eine sich schliessende Mischungslücke entdeckten.[6]

Bildungsenthalpien. Es liegt nahe, die in Form der Isothermen nach Abb. 4 geordneten Messergebnisse zur Berechnung von Bildungsenthalpien zuver wenden. Wir konnten dies nach dem Ansatz

$$\Delta H = R \cdot T_1 T_2 \cdot \frac{\ln K_{p_2} - \ln K_{p_1}}{T_2 - T_1}$$

durchführen. Für den Bereich $CeO_{1.50}$ und $CeO_{1.85}$ konnte diese Beziehung ohne weiteres angewendet werden, da zwischen $\ln K_p$ und $1/T$ im untersuchten Temperaturbereich für alle Zusammensetzungen eine lineare Funktion besteht.

In der Abbildung 5 ist dies für verschiedene herausgegriffene Zusammensetzungen belegt. Für den Bereich $CeO_{1.85}$–$CeO_{2.00}$ konnten wir dies nicht beweisen, da nur je zwei Messwerte zur Verfügung standen.

Die so berechneten partiellen Werte Δ^*H für die Bildungsenthalpien in Abhängigkeit von der Zusammensetzung der Oxyde können aus der Darstellung in Abbildung 6 abgelesen werden. Der Wert von Δ^*H ist naturgemäss für den heterogenen Bereich $CeO_{1.50}$–$CeO_{1.67}$ konstant. Im homogenen Bereich $CeO_{1.67}$–$CeO_{1.85}$ fällt er zunächst

bis $CeO_{1.80}$ langsam, zwischen $CeO_{1.80}$ und $CeO_{1.85}$ steiler ab. Bei $CeO_{1.85}$ scheint er ein Minimum zu durchlaufen und für höheren Sauerstoffgehalt wieder anzusteigen. Dieser Verlauf ist aber nicht sicher, weil in diesem Bereich der Zusammensetzung der Bodenkörper bei tiefen Temperaturen heterogen, bei hohen homogen ist und die Phasentrennung in die Energiebilanz mit eingehen muss. Zur Klärung dieser Frage sind weitere Messungen, insbesondere in der Nähe der Zusammensetzung $CeO_{2.0}$ erforderlich.

Eine Integration über den Gesamtverlauf der partiellen Bildungsenthalpien lässt sich mit voller Sicherheit für die Reaktion

$$4\,CeO_{1.50} + 0.7\,O_2 = 4\,CeO_{1.85}$$

ausführen und ergibt den Wert $\Delta H = -135 \pm 3$ kcal (für eine mittlere Temperatur von 850°C). Dies entspricht einer mittleren Bildungsenthalpie von -193 kcal/Mol O_2. Die Unsicherheit über den Verlauf der Enthalpiekurve zwischen $CeO_{1.85}$ und $CeO_{2.00}$ verbietet vorläufig eine exakte Ausdehnung der Berechnung bis zum Dioxyd. Benützt man als Näherung in diesem Bereich den für $CeO_{1.85}$ ermittelten minimalen Wert, so erhält man für die Gesamtwärmetönung der Reaktion

$$2\,Ce_2O_3 + O_2 = 2\,CeO_2$$

den Wert $\Delta H = -188.5$ kcal als unteren Grenzwert. Wir schätzen, dass er sich bei genauerer Kenntnis des Gebiets der sauerstoffreichsten Oxyde höchstens um 5 kcal erhöhen kann.

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ÜBER DIE OXYDE DES CERS—V*[1]

HOCHTEMPERATUR-RÖNTGENUNTERSUCHUNGEN AN CEROXYDEN

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Abstract—Samples of cerium oxide with a composition from $CeO_{2.00}$ to $CeO_{1.70}$ are examined by high temperature X-ray diffraction between 20 and 1000°C. From these experiments the phase relationship in this region is fully explained for the first time. All phase transitions occur very rapidly. The composition of the phase boundaries changes considerably with the temperature, in particular a miscibility gap, which has the boundaries $CeO_{2.00}$ and $CeO_{1.81}$ at room temperature, contracts with rising temperature, and closes at 685°C and at a composition of $CeO_{1.93}$. At higher temperatures a homogenous series of mixed crystals with cubic fluorite structure exists as is predicted for such a system. A summarizing discussion is given for the system of the cerium oxides, including the measurements of oxygen dissociation pressure.

IN einer vorhergehenden Arbeit[1] konnten wir zeigen, dass bei Ceroxyden des Bereichs $CeO_{2.00}$–$CeO_{1.81}$ oberhalb einer Temperatur von etwa 700°C der Sauerstoffzersetzungsdruck bei gegebener Temperatur mit der Zusammensetzung des Ceroxyds variabel ist. Dem Gibbs'schen Phasengesetz zufolge müsste in solchen Präparaten oberhalb 700°C nur eine einzige homogene Phase vorliegen.

Dies steht jedoch im Widerspruch zu den röntgenographischen Befunden von BRAUER und GRADINGER[2], sowie von BEVAN[3], die übereinstimmend fanden, dass bei ihren Präparaten in dem genannten Bereich stets zwei Phasen nebeneinander auftreten, und zwar die im kubischen Fluoritgitter kristallisierende α-Phase, $CeO_{2.00}$ und die β-Phase $CeO_{1.81}$, die gemäss BEVAN in einem nahe verwandten rhomboedrischen Gitter kristallisiert. Trotz Gleichheit der Grenzzusammensetzung bei $CeO_{1.81}$ liegen über die Zahl und Struktur der Phasen im Gebiet $CeO_{1.81}$–$CeO_{1.65}$ scheinbar verschiedene Angaben vor. In den Befunden von BRAUER und GRADINGER tritt nur eine einzige Phase mit Fluoritstruktur und variabler Gitterkonstante auf, während BEVAN drei diskrete Phasen beobachtete, die eine dem Fluoritgitter verwandte Struktur aber niedrigere Symmetrie besitzen. Übereinstimmung herrscht lediglich darin, dass bei beiden Untersuchungen an der sauerstoffarmen Grenze dieses Zwischengebiets kubische Gitterstruktur vorliegt.

Auch von uns konnte der röntgenographische Befund der Zweiphasigkeit im Bereich $CeO_{2.00}$–$CeO_{1.81}$ an Präparaten reproduziert werden, die unter Gleichgewichtsbedingungen oberhalb 700°C hergestellt waren, also homogen sein sollten. Diesen Widerspruch kann man nur durch die Annahme lösen, dass oberhalb etwa 700°C eine homogene Phase existiert, die sich beim Abschrecken und weiterem Behandeln bei Zimmertemperatur in die beobachteten zwei Phasen trennt. Dieses

* Der Inhalt dieser Arbeit wurde in gekürzter Form auf dem Annual Meeting of the American Ceramic Society in Chicago am 19. Mai 1959 vorgetragen.

[1] IV. Mitteilung: G. BRAUER u. K. A. GINGERICH, *J. Inorg. Nucl. Chem.* **16**, 77 (1960).
[2] G. BRAUER u. H. GRADINGER, *Z. Anorg. Chem.* **277**, 89 (1954).
[3] D. J. M. BEVAN, *J. Inorg. Nucl. Chem.* **1**, 49 (1955).

Verhalten erscheint überraschend, da sonst als sicher gilt, dass bei Oxydsystemen Hochtemperaturmischphasen abgeschreckt werden können, ohne dass dabei Entmischung in zwei Phasen auftritt. Es wurde vielfach die Erfahrung gemacht, dass zum Erreichen des Gleichgewichts in heterotypen Mischkristallen zwischen Dioxyden und Sesquioxyden der Seltenen Erden selbst bei so hoher Temperatur wie etwa 1400°C mehrere Stunden oder sogar Tage notwendig sind. Umwandlungen bei niederen Temperaturen sollten daher ausserordentlich langsam verlaufen.

Bei dieser Sachlage schien uns eine Klärung für die Ceroxyde am besten durch Beobachtungen der Phasenverhältnisse unmittelbar bei erhöhten Temperaturen erreichbar. Wir verwendeten eine heizbare Pulverkamera und sorgten dafür, dass sich die chemische Zusammensetzung der Untersuchungsproben während aller Temperaturbehandlungen nicht ändern konnte.

EXPERIMENTELLES

Als Ausgangsmaterial für die Versuche diente reinstes Cerdioxyd wie es auch in einer vorhergehenden Arbeit verwendet wurde.[1] Für jeden Versuch wurde etwa 1 g verwendet.

Die Reduktion des Cerdioxyds bis zu einer bestimmten Zusammensetzung erfolgte mittels eines Wasserstoff-Wasserdampf-Gemisches unter bekannten Gleichgewichtsbedingungen und in derselben Apparatur, die für die Gleichgewichtsbestimmungen verwendet worden war.[1] Bei einigen Präparaten wurde statt dessen mit trockenem Wasserstoff bei einer vorher empirisch ermittelten Temperatur während fünf Stunden reduziert. In beiden Fällen wurde das reduzierte Präparat unter Wasserstoff abgeschreckt und mit seinem Schiffchen in ein an die Apparatur mit Schliffen angeschlossenes Verteilungsrohr geschoben. Dieses Rohrstück besass seitlich angeschlossene Röntgenkapillaren und gegenüberliegend verschliessbare Öffnungen zum Einführen dünner Hantierungsgeräte. Dort wurde die Abfüllung des Ceroxyds in die Röntgenkapillaren aus Quarzglas mit 0·01 oder 0·02 mm Wandstärke und 0·5 bis 0·7 mm Durchmesser vorgenommen. Obgleich die Quarzkapillaren vor der Verwendung ausgeglüht wurden, blieb beim Einfüllen stets ein dünner Ceroxydfilm an der inneren Wandung haften. Dieser Film musste mittels einer dünnkieligen Vogelfeder entfernt werden, um nachher eine völlig saubere vakuumdichte Abschmelzstelle zu erhalten. Die ganze Abfülloperation erfolgte unter Luftausschluss. Dann wurde auf etwa 10^{-3} mm Hg evakuiert und die Quarzkapillare unter diesem Vakuum abgeschmolzen. Das verschlossene Röhrchen mit dem Röntgenpräparat wurde mehrere Stunden an Luft bei etwa 850°C getempert. Hielt das Röhrchen bei dieser Temperatur die Druckdifferenz von einer Atmosphäre aus, ohne dass eine Aufhellung des blauen Ceroxyds durch Eindringen von Luft beobachtet wurde, so war das Präparat für eine Aufnahmeserie in der Hochtemperaturkamera geeignet und wurde hierzu mittels eines reversiblen Kitts in einem geeigneten Präparatenträger zentrisch befestigt.

Der im Schiffchen verbliebene Rest des Präparats wurde unter Stickstoff gewogen und dann zu CeO_2 oxydiert. Aus der Gewichtsdifferenz konnte die genaue Zusammensetzung des abgefüllten Ceroxyds bestimmt werden.

Bei einigen Präparaten des Bereichs $CeO_{2\cdot00}$–$CeO_{1\cdot68}$ wurde das Einfüllen in die Quarzmarkröhrchen an Luft vorgenommen. In diesem Zusammensetzungsbereich verläuft die Autoxydation so langsam, dass sie bequem auf der Waage verfolgt werden konnte. Da gleichzeitig keine Störung durch Hygroskopizität der Ceroxyde feststellbar war, konnte die Zusammensetzung des eingefüllten Ceroxyds rechnerisch genau bestimmt werden.

Für die röntgenographischen Untersuchungen bei höheren Temperaturen wurde eine von der Firma Seemann (Heidelberg) hergestellte heizbare Pulverkamera von 12 cm Durchmesser verwendet. Bei dieser Kamera gestattet die Heizwicklung aus Platindraht Arbeiten bis zu Temperaturen von etwa 1300°C unter Vakuum. Der Film befindet sich innerhalb der Vakuumglocke. Eine besondere Vorrichtung ermöglicht sechs verschiedene Diagramme nacheinander auf einem Film aufzunehmen, ohne dass die Kamera geöffnet werden muss. Die Zentrierung des Präparats und seine Beobachtung während einer Aufnahme sind leicht möglich. Die Temperatur wird mittels eines Pt/Pt-Rh-Thermoelements gemessen, dessen Lötstelle sich einen halben Millimeter unterhalb des Röntgenpräparats befindet.

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Für die Aufnahmen verwendeten wir mit Nickel gefilterte CuK_α-Strahlung (K_α = 1·5418 Å, K_{α_1} = 1·5405 Å, K_{α_2} = 1·5443 Å). Die Belastung der Röhre betrug 25 kV und 32 mA. Während der Aufnahmen wurde die Kamera bis auf etwa 10^{-1} bis 10^{-2} mm Hg evakuiert. Mittels eines Energiereglers wurde eine Konstanz und eine Messgenauigkeit der Temperatur von ±10°C bei etwa 1000°C erreicht. Die Raumtemperatur bei allen Aufnahmen betrug 20 ± 3°C. Die Belichtungsdauer für eine Aufnahme variierte bei den reduzierten Ceroxyden von 10 bis 35 Stunden. Lange Belichtungszeiten waren vor allem dann notwendig, wenn die Linien einer Phase beobachtet werden sollten, welche nur in untergeordneter Menge im Präparat vorlag. Vor Beginn einer Aufnahme wurden die Präparate in der Kamera in der Regel drei Stunden bei der Aufnahmetemperatur gehalten. Diese Massnahme diente gleichzeitig der Sicherung der Gleichgewichtseinstellung und einer Verbesserung der Linienschärfe auf den Diagrammen. In Hinsicht auf den letztgenannten Effekt erforderte das Präparat $CeO_{1.797}$ Temperzeiten von 20 bis 30 Stunden.

Die verwendeten verschlossenen Quarzkapillaren eigneten sich deshalb besonders gut als Träger für die bei erhöhten Temperaturen hoch sauerstoffempfindlichen reduzierten Ceroxyde, weil in ihrem relativ kleinen abgeschlossenen Raum die Gefahr für eine Sauerstoffaufnahme zu vernachlässigen ist. Bezüglich der chemischen Resistenz von Quarzglas stellten wir in Vorversuchen fest, dass es von den Ceroxyden bei 1000°C langsam angegriffen wurde. Dieser Angriff ist besonders bei Cerdioxyd stark, wenn Luft zutreten kann, aber wesentlich schwächer, wenn das Präparat im Vakuum abgeschmolzen war. Da der Angriff im letzten Falle erst nach mehr als zehn Stunden begann, liessen sich die Röntgenaufnahmen selbst bei 1000°C noch ohne wesentliche Störung durchführen. Bei 900°C und bei tieferen Temperaturen spielte die Reaktion zwischen Trägerröhrchen und Oxydpräparat keine Rolle mehr. Eine weitere Störung liegt in der Entglasung der Quarzkapillaren, die bei mehr als 100-stündiger Versuchsdauer oberhalb 900°C beobachtet wurde. Offensichtlich wird die Geschwindigkeit der Entglasung durch die Einwirkung der Röntgenstrahlen begünstigt. Kapillaren von 0·02 mm Wandstärke erwiesen sich wesentlich resistenter gegen Entglasung als die üblichen von 0·01 mm. Die damit verbundene, etwas längere Expositionsdauer nahmen wir in Kauf. In allen Fällen prüften wir nach einer Versuchsreihe die Unversehrtheit des Präparates.

Eine Präzisionsbestimmung der Gitterkonstanten bei höheren Temperaturen war dadurch erschwert, dass die Konstruktion der Kamera nur symmetrische Aufnahmen gestattete. Wir mussten deshalb eine Eichsubstanz mit genau bekannter Gitterkonstante verwenden. Als solche bot sich das Ausgangsmaterial, Cerdioxyd an. Es wurde in gleicher Weise in eine Quarzkapillare eingeschmolzen, wie die zu untersuchenden reduzierten Präparate. Auf einem einzigen Film nahmen wir in der Regel ein Eichdiagramm von CeO_2 bei 20°C und bis zu fünf Temperaturdiagramme einer reduzierten Probe auf. Dazu musste lediglich das Präparat ausgewechselt werden, während die Lage des Films im Filmhalter unverändert blieb. Mit Hilfe der Eichaufnahme konnte für alle Winkelwerte die Filmkorrektur bestimmt werden. So brauchte auch die Abhängigkeit der Absorption vom θ-Wert wegen der Gleichartigkeit der Präparate nicht berücksichtigt zu werden. Ebenso konnten geringfügige Unsymmetrien in einzelnen Bereichen des Röntgenfilms eliminiert werden. Auf einen Fehler der durch das Verschieben des Filmhalters auftreten könnte, wurde besonders geprüft. Ein solcher systematischer Fehler in der Konstruktion der Kamera war nicht feststellbar. Die weiteren Fehlerquellen, wie Ungenauigkeit in der Temperaturmessung, Ungenauigkeit in der Vermessung des Filmes, die Unschärfe der Reflexe und die Unterschiede in den Präparatedurchmessern konnten abgeschätzt werden. Danach lassen sich die Gitterkonstanten mit folgender Genauigkeit angeben: 0·002 Ångström-Einheiten für Cerdioxyd und die α-Phase, sofern dieselbe in den Präparaten überwiegt, und 0·003 Ångström-Einheiten für die meisten anderen Werte. Die Gitterkonstanten der β-Phase beziehen sich auf die pseudokubische Indizierung der Reflexe. Die Genauigkeit beträgt hier nur 0·003–0·005 Å. Ein ebenso grosser Fehler wird für die Aufnahmen Nr. 33 und 46–59 (vgl. Tabelle 1) geschätzt, weil hier die CeO_2-Eichaufnahmen auf den Filmen fehlen. Die Gitterkonstanten berechneten wir in der Regel aus den Abständen der Reflexe mit K_{α_1}–K_{α_2}-Aufspaltung: 620, 533 und 622. Zuweilen mussten auch andere Reflexe wie 531, 511 + 333, 422, 420 und 311 herangezogen werden.

ERGEBNISSE UND DISKUSSION

Die röntgenographischen Befunde an den mit der Hochtemperaturkamera untersuchten Ceroxyden des Bereichs $CeO_{2.00}$–$CeO_{1.81}$ sind in Tabelle 1 in abgekürzter Form enthalten. Die Tabelle enthält Aussagen über die relative Intensität einzelner

TABELLE 1.—REFLEXINTENSITÄT IN DEN RÖNTGENDIAGRAMMEN UND GITTERKONSTANTEN DER CEROXYDE DES BEREICHS $CeO_{2.00-1.81}$ BEI VERSCHIEDENEN TEMPERATUREN

Nr.	Formel	Temperatur (°C)	Intensität und Gitterkonstante*				
			Phase I (α-Phase)		Phase II (β oder α′-Phase)		
1	$CeO_{2.000}$	20	*st*	5·411†	—	—	—
2		300	*st*	5·429	—	—	—
3		460	*st*	5·440	—	—	—
4		550	*st*	5·443	—	—	—
5		610	*st*	5·448	—	—	—
6		710	*st*	5·456	—	—	—
7		890	*st*	5·466	—	—	—
8		900	*st*	5·467	—	—	—
9	$CeO_{1.999}$	450	*st*	5·442	*ss*	—	—
11		710	*st*	5·465	—	—	—
12	$CeO_{1.988}$	20	*st*	5·412	*s*	—	β
13		300	*st*	5·430	*s*	—	—
14		400	*st*	5·437	*s*	—	—
15		500	*st*	5·448	*ss*	—	—
16		700	*st*	5·468	—	—	—
19	$CeO_{1.918}$	20	*st*	5·411	*m*	5·499	β‡
20		450	*st*	—	*m*	5·519	α′
21		500	*st*	5·445	*m*	5·514	α′
22		550	*st*	5·452	*st*	5·513	α′
23		600	*st*	—	*st*	—	α′
24		650	*st*	—	*st*	—	α′
25		700	*st*	—		α′ identisch mit α	
26		730	*st*	5·494		α′ identisch mit α	
27		900	*st*	5·509		α′ identisch mit α	
28		900	*st*	5·510		α′ identisch mit α	
29		900	*st*	5·509		α′ identisch mit α	
30	$CeO_{1.898}$	20	*m*	5·412	*st*	—	β
31		510	*m*	5·450	*st*	5·516	α′
32		610	*s*	5·462	*st*	5·512	α′
33		660	*ss*	5·480	*st*	5·506	α′
34	$CeO_{1.845}$	20	*m*	—	*st*	5·497	β
35		20	*m*	—	*st*	5·498	β
36		300	*m*	—	*st*	5·514	β
37		400	*m*	—	*st*	5·521	β
38		440	*s*	—	*st*	—	α′
39		470	*ss*	—	*st*	—	α′
40		490	*ss*	—	*st*	—	α′
41		510	—	—	*st*	5·514	α′
42		700	—	—	*st*	5·527	α′
43		900	—	—	*st*	5·539	α′
44	$CeO_{1.840}$	20	*s*	—	*st*	—	β
45		400	*ss*	—	*st*	5·518	β
46		600	—	—	*st*	5·535	α′
47		800	—	—	*st*	5·546	α′
48		900	—	—	*st*	5·554	α′
49		1000	—	—	*st*	5·565	α′
53	$CeO_{1.820}$	20	*ss*	—	*st*	—	β
54		250	*ss*	—	*st*	—	β
55		545	—	—	*st*	—	α′

* Intensität: *st* = stark, *m* = mittel, *s* = schwach, *ss* = sehr schwach.

† Diese Gitterkonstante wurde durch Präzisionsmessung nach der asymmetrischen Methode mit Hilfe einer Seemannkamera (57·3 mm ϕ) bestimmt und diente als Bezugswert für alle aus Hochtemperaturaufnahmen berechneten Gitterkonstanten.

‡ Die Gitterkonstanten der β-Phase beziehen sich auf die pseudokubische Indizierung der Reflexe.

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Linienmuster beim Auftreten zweier Phasen, sowie einzelne Messdaten von Gitterkonstanten. Die Angaben sind nach zunehmendem Reduktionsgrad des Ceroxyds und nach steigender Temperatur t geordnet. Doppelte Angaben für dieselbe Zusammensetzung und Temperatur resultieren aus verschiedenen, getrennt durchgeführten Röntgenaufnahmen. Die Angaben der relativen Intensitäten beziehen sich auf die Reflexe 220, 311, 222, 400, 321, 420 und 511 + 333.

Beschreibung der Linienmuster

In dem Zweiphasengebiet $CeO_{2\cdot00}$–$CeO_{1\cdot81}$ treten auf den bei Zimmertemperatur hergestellten Röntgendiagrammen die Linien der kubischen α-Phase ($CeO_{2\cdot00}$) und der rhomboedrischen β-Phase ("Zwischenphase",[2] $CeO_{1\cdot81}$) nebeneinander auf. Dabei nimmt die relative Intensität der Reflexe der α-Phase mit fallendem Sauerstoffgehalt im Ceroxyd ab, während die Intensität der Reflexe der β-Phase gleichzeitig grösser wird. Die rhomboedrische Struktur der β-Phase zeigte sich auf unseren Röntgenfilmen in einer Verbreiterung und Unschärfe der Reflexe, die mit wachsenden θ-Werten zunimmt. Eine Aufspaltung der kubischen Linien in die rhomboedrischen ist auch bei dem relativ grossen Radius unserer Hochtemperaturkamera von etwa 12 cm noch nicht zu beobachten.

Aus diesem Befund lässt sich der eingangs erwähnte Unterschied in den Befunden verschiedener Autoren bezüglich der Struktur der β-Phase erklären. Das Auflösungsvermögen der von BRAUER und GRADINGER gebrauchten Aufnahmevorrichtung und die Zahl der untersuchten Proben reichte nicht aus, um die Phasenverhältnisse in allen Einzelheiten zu erkennen.

Allgemein und auch bei höheren Temperaturen konnten wir feststellen, dass die Untergrundschwärzung auf den Röntgenfilmen mit wachsendem Reduktionsgrad und mit wachsenden θ-Werten zunimmt. Gleichzeitig beobachteten wir, dass die Reflexe der α-Phase relativ und absolut stärker hervortraten als die der β-Phase, so dass zum Beispiel bei Mischungen mit gleichen Anteilen der beiden Phasen die Reflexe der α-Phase intensitätsmässig dominierten, besonders bei hohen θ-Werten.

Gegenüber den Beobachtungen bei Zimmertemperatur ändert sich das Erscheinungsbild der Röntgendiagramme, wenn man zu höheren Temperaturen übergeht. Für zwei charakteristische Präparate $CeO_{1\cdot848}$ und $CeO_{1\cdot915}$ geben wir in den Abbildungen 1 und 2 schematisch diese Veränderungen wieder. Die Interferenzlinien der Pulverdiagramme werden durch Striche wiedergegeben, deren Länge ein Mass für die Linienintensität darstellt. Linienverbreiterungen und Koinzidenzen sind gleichfalls schematisch berücksichtigt.

In der Abbildung 1 ist das Temperaturverhalten des Präparats $CeO_{1\cdot848}$ dargestellt. Das Diagramm einer bei 20°C durchgeführten Eichaufnahme von CeO_2 ist ebenfalls in die Abbildung aufgenommen. Man ersieht, dass bei 400°C die Linien der α-Phase gegenüber der Aufnahme bei 20°C geringfügig geschwächt sind. Zwischen 400°C und 440°C wandelt sich das rhomboedrische Gitter der β-Phase in ein kubisches, fluoritähnliches Gitter um. Dieses Gitter gleicht offenbar dem der α-Phase vollkommen bis auf die etwas veränderte Gitterkonstante. Die zugehörige Phase soll daher mit α′ bezeichnet werden. Die Umwandlung $\beta \rightarrow \alpha'$ kennzeichnet sich in dem Diagramm besonders durch die klare Dublett-Aufspaltung der Reflexe 531, 600 + 442, 620, 533 und 622. Die rhomboedrische β-Phase zeigt diese Aufspaltung nicht und ist dadurch auf den Hochtemperaturdiagrammen am besten gekennzeichnet.

Oberhalb einer Temperatur von 440°C stehen also 2 Phasen mit kubischer Struktur miteinander im Gleichgewicht. Die Reflexe der α-Phase werden mit zunehmender Temperatur immer schwächer und verschwinden zwischen 490 und 500°C. Oberhalb 510°C ist ein Oxydpräparat der Zusammensetzung $CeO_{1.848}$ einphasig und besitzt Fluoritstruktur. Weitere Aufnahmen bei noch höheren Temperaturen, die in der Abbildung nicht dargestellt sind, beweisen, dass dieser Zustand sich bis mindestens 1000°C nicht mehr ändert.

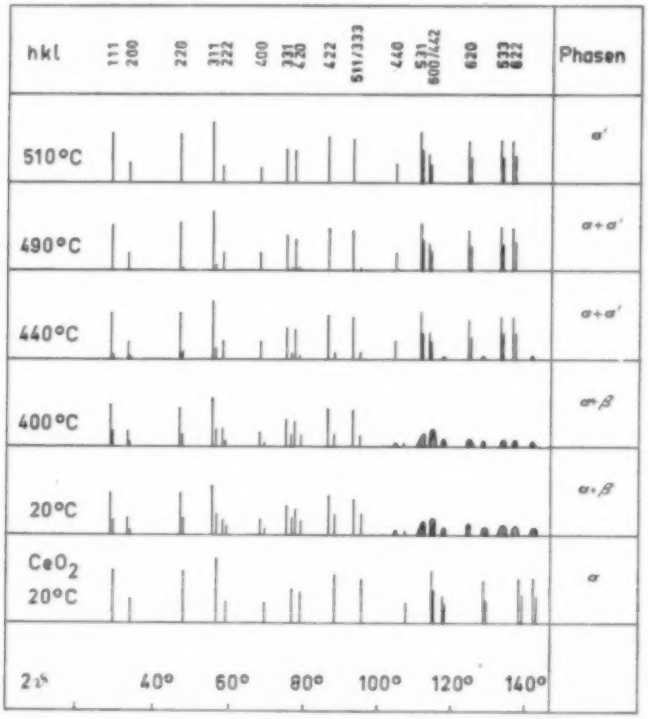

ABB. 1.—Temperaturverhalten eines Ceroxydpräparats $CeO_{1.848}$, wiedergegeben durch schematische Darstellung der Röntgendiagramme.

Die Abbildung 2 stellt das Temperaturverhalten des Präparats $CeO_{1.915}$ dar. Die Zusammensetzung dieses Präparates entspricht dem mittleren Bereich der Mischungslücke zwischen $CeO_{2.00}$ und $CeO_{1.81}$ bei 20°C. Die Linienintensitäten dieser beiden anwesenden Phasen ändern sich relativ zueinander etwas mit der Temperatur. Dies lässt darauf schliessen, dass sich die Mengenverhältnisse der beiden Phasen mit der Temperatur verschieben.

Noch aufschlussreicher als die Betrachtung der Intensitätsverhältnisse ist die Änderung der Lage der Reflexe der beiden Phasen α und α′ bei verschiedenen Temperaturen. Schon in der Aufnahme bei 450°C lässt sich gegenüber 20°C eine Annäherung der einander entsprechenden Reflexe der beiden Phasen erkennen, besonders wenn man das Linienquartett der Reflexpaare 331 und 420 betrachtet. Diese Annäherung verstärkt sich mit steigender Temperatur, bis schliesslich bei 700°C nur die Reflexe einer einzigen Phase mit Fluoritstruktur vorhanden sind. Bei 700°C

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ist diese Fluoritphase allerdings noch gestört; die Reflexe mit den höchsten Indices zeigen noch keine Dublett-Aufspaltung. Bei 730°C ist aber diese Störung nicht mehr auf dem Röntgendiagramm sichtbar. Mit steigender Temperatur werden also die Gitterkonstanten der α- und der α′-Phase immer ähnlicher, die Ausdehnung des Zweiphasengebiets verkleinert sich, und bei etwa 700°C schliesst sich die Mischungslücke. Gleichzeitig lässt sich aus der annähernd gleich grossen Intensität der Reflexe der beiden Phasen vor dem Übergang in das homogene Gebiet schliessen,

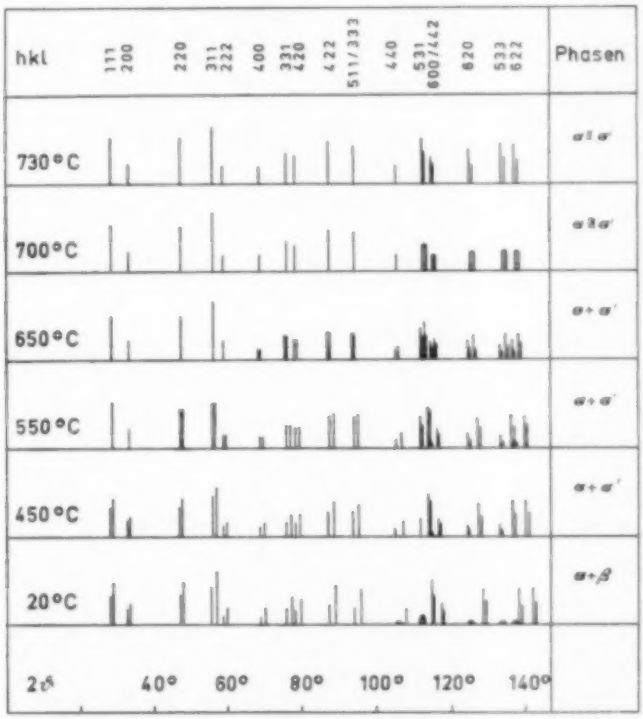

Abb. 2.—Temperaturverhalten eines Ceroxydpräparats $CeO_{1.915}$, wiedergegeben durch schematische Darstellung der Röntgendiagramme.

dass das Temperatur-Maximum der Mischungslücke gerade etwa bei der Zusammensetzung dieses in der Abbildung 2 behandelten Oxydpräparats $CeO_{1.915}$ liegt.

Bei Präparaten, deren Zusammensetzung von dem Maximum der Mischungslücke entfernt liegt, wie z.B. bei $CeO_{1.848}$, findet dieses Identischwerden der beiden Phasen mit steigender Temperatur nicht statt. In diesen Fällen werden die Reflexe derjenigen Phase, die in geringerer Menge vorliegt, vor Erreichen der Temperatur, bei welcher das Oxydpräparat homogen wird, rasch schwächer und verschwinden. Solange beide Phasen vorhanden sind, haben die Reflexe den Abstand, der den Phasengrenzen bei der Aufnahmetemperatur entspricht. So lässt sich bei dem in Abbildung 1 dargestellten $CeO_{1.848}$ verfolgen, wie die α-Phase verschwindet, noch ehe α- und α′-Phase identisch geworden sind. Für Präparate mit anderen Zusammensetzungen lässt sich ein entsprechendes Verhalten in gleicher Weise aus Intensitätsangaben der Tabelle 1 ableiten.

Die Temperaturabhängigkeit der Gitterkonstanten a bestimmten wir für CeO_2 zwischen 20 und 900°C, für $CeO_{1\cdot848}$ und $CeO_{1\cdot840}$ zwischen 500 und 1000°C. Die Beschränkung auf diesen Bereich erfolgte, weil hier diese reduzierten Ceroxyde einphasig sind und in der kubischen Form vorliegen. Die Werte für die Gitterkonstanten sind in Tabelle 1 enthalten (CeO_2 Nr. 1–9; $CeO_{1\cdot848}$ Nr. 41–43; $CeO_{1\cdot840}$ Nr. 46–49). Aus diesen Werten ergibt sich innerhalb der Genauigkeit der Bestimmung eine lineare Abhängigkeit mit der Temperatur, sowohl für CeO_2 als auch für die reduzierten Ceroxyde. Die Steigung der Geraden $\Delta a/\Delta t$ ist für CeO_2 und die reduzierten Proben identisch und beträgt $6{\cdot}4 \times 10^{-5}$ Å/grad. Der mittlere lineare Ausdehnungskoeffizient berechnet sich hieraus für die angegebenen Temperaturbereiche zu $11{\cdot}8 \times 10^{-6}$ grad^{-1}.

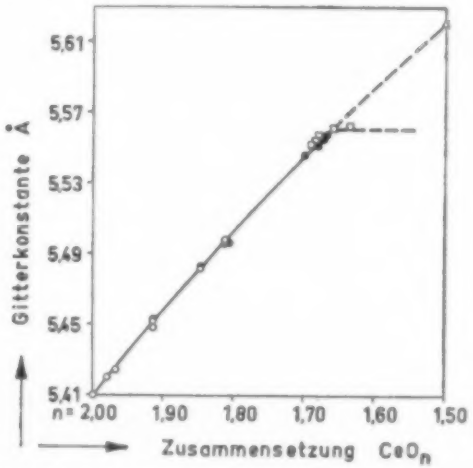

ABB. 3.—Abhängigkeit der Gitterkonstante von der Zusammensetzung bei kubischen Ceroxyden; von höheren Beobachtungstemperaturen umgerechnet auf 20°C.

Mit Hilfe dieses neu bestimmten Ausdehnungskoeffizienten rechneten wir die Gitterkonstanten von einphasigen kubischen Hochtemperaturpräparaten des Bereichs $CeO_{2\cdot00}$–$CeO_{1\cdot81}$ von der Beobachtungstemperatur auf Raumtemperatur um. Die für 20°C resultierenden Gitterkonstanten sind in Abbildung 3 in Abhängigkeit von der Zusammensetzung der Oxyde dargestellt. Zusätzlich wurden die für 20°C bestimmten Werte Nr. 19, 34 und 35 für die β-Phase aus Tabelle 1 eingetragen. In der Abbildung sind ferner die von BRAUER und GRADINGER[2] und von BEVAN[3] bestimmten Werte für die Gitterkonstanten im homogenen Bereich der "Zwischenphase" mit C-Sesquioxydstruktur aufgenommen, sowie ein extrapolierter Wert für kubisches $CeO_{1\cdot5}$ aus einer nicht veröffentlichten Untersuchung der beiden zuerst genannten Autoren.[4]

Aus der Darstellung in Abbildung 3 ersieht man, dass im Bereich der bekannten Mischungslücke die auf 20°C umgerechneten Gitterkonstanten mit ausgezeichneter Übereinstimmung auf der Kurve liegen, die BRAUER und GRADINGER für einen angenommenen kontinuierlichen Übergang Cerdioxyd-kubisches Cersesquioxyd aus den Gitterkonstanten der reinen Oxyde berechnet haben. Innerhalb des homogenen Bereichs der "Zwischenphase" liegen die von den beiden Autoren und die von BEVAN gemessenen Gitterkonstanten ebenfalls auf dieser berechneten Kurve. Das bei Zimmertemperatur verifizierbare Stück $CeO_{1\cdot69}$–$CeO_{1\cdot65}$ dieser Kurve stellt demnach

[4] H. GRADINGER, Dissertation, Universität Freiburg/Brg. (1952).

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offensichtlich einen Teil einer längeren Mischungsreihe dar, die ihren Ausgangspunkt von Cerdioxyd nimmt.

Bestimmung der Grenzen der Mischungslücke

Die Kenntnis der Abhängigkeit der Gitterkonstanten von der Temperatur und von der Zusammensetzung benützten wir zur Bestimmung der Grenzen der Mischungslücke aus den zugehörigen Gitterkonstanten. Bei Pulverdiagrammen, in denen das betreffende Ceroxyd zweiphasig erscheint, entspricht die zu jeder Phase gehörende Gitterkonstante einer Grenzzusammensetzung bei der Aufnahmetemperatur. Daran, dass sich das Phasengleichgewicht oberhalb 300°C während der Aufnahmezeit rasch einstellt, können wir auf Grund unserer Erfahrungen nicht zweifeln. Es spricht nichts gegen die Annahme, dass das Phasengleichgewicht auch unterhalb 300°C noch hinreichend rasch erreicht wird.

Im allgemeinen rechneten wir die in Tabelle 1 für t°C angegebenen Gitterkonstanten von zweiphasigen Präparaten auf 20°C um. Aus der in Abbildung 3 dargestellten Abhängigkeit dieser berechneten Gitterkonstanten von der Zusammensetzung wurden dann die Grenzzusammensetzungen der Phasen graphisch ermittelt.

Ausser dieser Methode liess sich für den besonderen Fall der α-Phase im Temperaturbereich von 20–500°C noch eine andere Bestimmungsmethode mit höherer Genauigkeit anwenden. Dazu nahmen wir auf einem Film bei der gleichen Temperatur die Diagramme von reinem Cerdioxyd und einem schwach reduzierten, jedoch noch zweiphasigen Oxyd auf. Aus der mit hoher Genauigkeit bestimmbaren Differenz der beiden genannten Gitterkonstanten konnten wir mit Hilfe der bekannten Abhängigkeit der Gitterparameter von der Zusammensetzung (Abb. 3) den Grenzpunkt des Homogenitätsbereiches der α-Phase ermitteln. Durch Anwendung dieses Verfahrens auf verschiedene Temperaturen erhielten wir die gesamte Grenzkurve zwischen 20 und 500°C. Weil die Grenzzusammensetzungen der α-Phase in diesem Temperaturbereich nur sehr wenig von der des reinen Cerdioxyds abweichen, verschwinden bei dieser Bestimmungsmethode alle systematischen Fehler.

Eine dritte Möglichkeit zur Bestimmung der Phasengrenzen lässt sich darauf gründen, dass die Mengenverhältnisse der beiden koexistierenden Phasen aus ihren Röntgenintensitäten abgeschätzt werden können. Bei dieser Abschätzung muss die früher erwähnte Abhängigkeit des Streuvermögens vom Reduktionsgrad der Ceroxyde berücksichtigt werden. Ausser den Mengenverhältnissen benötigt man noch die Differenz der Gitterkonstanten beider Phasen und die Bruttozusammensetzung des Gesamtpräparates. Aus der Differenz der Gitterkonstanten wird die Differenz der Zusammensetzung der beiden Phasen mit Hilfe der Funktion aus Abbildung 3 festgelegt. Dieser Betrag wird nach den geschätzten Mengenverhältnissen dem Hebelgesetz entsprechend so aufgeteilt, dass die Bruttozusammensetzung den Schwerpunkt bildet. Diese Methode wurde auf die Probe $CeO_{1\cdot915}$ und die Temperaturen 600 und 650°C angewendet, wo die Voraussetzungen für diese Berechnungsart besonders günstig waren.

In Abbildung 4 sind die nach den verschiedenen Methoden ermittelten Werte für die Grenzzusammensetzung eingetragen. Sie fügen sich zu einem Kurvenzug zusammen, der die Begrenzung der Mischungslücke darstellt.

Aus dem Bereich $CeO_{1\cdot81-1\cdot70}$, in welchem bei tiefen Temperaturen mehrere rhomboedrische Phasen existieren, wurden die Verhältnisse am Ceroxydpräparat $CeO_{1\cdot787}$ besonders geprüft. Die Zusammensetzung dieses Präparats entspricht dem Zweiphasengebiet, in dem die rhomboedrischen Phasen β und γ nebeneinander vorliegen (siehe Abbildung 4). Zu der Durchführung der Röntgenaufnahmen in dieser Reihe waren Belichtungszeiten zwischen 30 und 40 Stunden notwendig. Bei den meisten Röntgendiagrammen erzielten wir durch vorheriges Tempern von 20–30 Stunden bei der Aufnahmetemperatur eine Verschärfung der Reflexe.

In den Pulverdiagrammen bei 20°C (Nr. 61–63) ist die Trennung der Linien der β- und der γ-Phase nicht deutlich erkennbar. Es sind lediglich sämtliche Reflexe breiter, als die entsprechenden der β-Phase in den früher besprochenen Diagrammen (Abb. 1 und 2). Nur bei den Reflexen mit den pseudokubischen Indices 422 und 600 + 442 ist eine Aufspaltung in zwei Linien entsprechend den beiden Phasen β und γ angedeutet. Auf den Filmen ist aber gleichzeitig die Untergrundschwärzung so gross, dass feine Unterschiede in den Konturen der höheren Reflexe nicht mit Sicherheit gedeutet werden können.

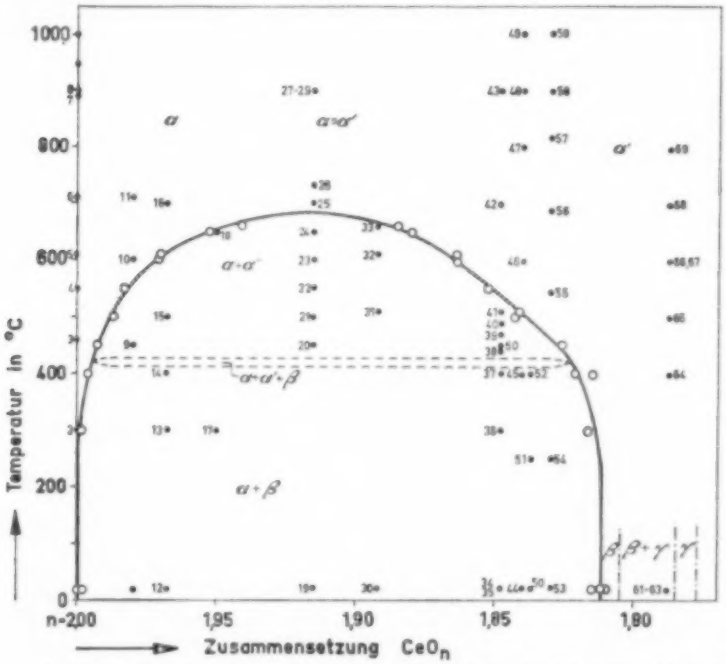

ABB. 4.—Phasendiagramm des Systems der Ceroxyde im Bereich $CeO_{2.00}$ bis $CeO_{1.80}$.

Beim Übergang zu den Temperaturen 400°C (Nr. 64), 500°C (Nr. 65) und 600°C (Nr. 66 und 67) beobachteten wir keine Änderung im Erscheinungsbild der Linienmuster gegenüber 20°C. Die bei den verschiedenen Temperaturen beobachtete Konstanz in den Linienkonturen könnte ein Hinweis dafür sein, dass die Grenzzusammensetzungen der beiden rhomboedrischen Phasen nicht wesentlich temperaturabhängig sind. Dieser Befund wiederum könnte als Stütze der Annahme von BEVAN gelten, dass diese Phasen geordnet sind. Auch die geringe Temperaturabhängigkeit der sauerstoffreichen Grenzzusammensetzung der β-Phase vor der Umwandlung in die α'-Phase (Abb. 4) würde mit dieser Deutung im Einklang stehen.

Beim Übergang von 600 auf 700°C ändert sich das Bild des Röntgendiagramms wesentlich. Bei 700°C liegt nur eine homogene Phase mit kubischer, fluorit-ähnlicher Struktur und scharfen Reflexen vor. Diese Umwandlung ist reversibel, wenn die Temperatur wieder auf 600°C gesenkt wird. Daraus folgt, dass die homogene Reihe der kubischen α-Mischkristalle oberhalb 700°C sich von $CeO_{2.00}$ bis mindestens $CeO_{1.78}$ erstreckt.

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Das Auflösungsvermögen unserer Kamera gestattete vorläufig nicht das Temperaturverhalten im Bereich $CeO_{1.81}$–$CeO_{1.65}$ genauer zu untersuchen.

Phasendiagramm

In der Abbildung 4 sind die von uns zwischen 20 und 1000°C aufgefundenen Phasenverhältnisse im Bereich $CeO_{2.00-1.78}$ graphisch dargestellt. Die Abbildung enthält die Repräsentationspunkte für den grösseren Teil der in dieser Arbeit untersuchten Oxydproben und deren Temperaturaufnahmen. Durch Nummerierung wird der Zusammenhang mit der Besprechung und mit der Tabelle 1 hergestellt. Das hier vorgeschlagene Phasendiagramm enthält als Hauptteil die in dieser Arbeit aufgefundene Grenzkurve der Mischungslücke zwischen α- und β-Phase. Ferner sind in der Abbildung für einen Teil des Bereichs $CeO_{1.81}$–$CeO_{1.69}$ die von BEVAN ermittelten Phasengrenzen eingezeichnet.

Wie aus der Abbildung 4 ersichtlich ist, besitzt die α-Phase (Cerdioxyd) zwischen 20 und 300°C nur einen extrem engen Homogenitätsbereich entsprechend den Grenzen $CeO_{2.000}$ und $CeO_{1.998}$. Dieser Bereich erweitert sich oberhalb 300°C rasch zunehmend nach der sauerstoffärmeren Seite hin, bis bei einer Zusammensetzung $CeO_{1.918}$ und bei 685°C das Maximum der Mischungslücke erreicht ist.

Für die β-Phase, welche nach BEVAN bei Zimmertemperatur ein Homogenitätsbereich von $CeO_{1.812}$ bis $CeO_{1.805}$ besitzt, erweitert sich dieser Bereich bei höheren Temperaturen bei 400°C in Koexistenz mit der α-Phase ebenfalls nur unwesentlich im Sinne einer Zunahme des Sauerstoffgehalts.

Zwischen 400 und 440°C erfolgt eine Umwandlung der rhomboedrischen β-Phase in die kubische fluoritähnliche α′-Phase. Die Existenz des zu erwartenden Dreiphasengebiets α-α′-β konnten wir nicht beobachten. Es muss im Temperaturbereich zwischen 400 und 440°C liegen. Die Möglichkeit seiner Begrenzung haben wir in der Abbildung mit gestrichelten Linien angedeutet.

Der Homogenitätsbereich der α′-Phase vergrössert sich unmittelbar oberhalb dieser Umwandlungstemperatur zu höheren Sauerstoffgehalten hin bis zum Maximum der Mischungslücke bei $CeO_{1.918}$ und 685°C. In diesem Maximum und bei allen höheren Temperaturen sind die α- und die α′-Phase miteinander identisch.

ZUSAMMENFASSENDE BETRACHTUNG ÜBER DAS SYSTEM DER CEROXYDE

Die vorstehend beschriebenen Untersuchungen in der Hochtemperaturkamera ermöglichen zusammen mit den Ergebnissen unserer vorhergehenden Untersuchung[1] eine Aufklärung des besonderen Verhaltens der Ceroxyde. Gleichzeitig können auch frühere Untersuchungen einbezogen und scheinbare Widersprüche gedeutet werden.

Für den Bereich $CeO_{2.00-1.81}$ ist charakteristisch, dass oberhalb 700°C eine lückenlose Reihe heterotyper Mischkristalle mit Fluoritstruktur und unterhalb 685°C eine Mischungslücke existiert, die sich mit fallender Temperatur verbreitert und bei Zimmertemperatur die Ausdehnung $CeO_{2.00-1.81}$ besitzt. Es hat sich gezeigt, dass sich die Festkörperphasengleichgewichte beim Abkühlen der einzelnen Versuchsproben so rasch einstellen, dass alle Untersuchungen bei Zimmertemperatur nur den Zustand unterhalb etwa 300°C wiedergeben und keine Rückschlüsse auf die Gleichgewichte bei beliebigen höheren Temperaturen gestatten, denen die Proben vorher ausgesetzt

waren. Mit diesem Tatbestand stimmen die Messungen der Sauerstoffzersetzungsdrucke vollkommen überein. Wie Abbildung 4 der vorausgehenden Veröffentlichung[1] zeigt, besitzt die Redox-Isotherme 600°C einen horizontalen Teil zwischen $CeO_{1.98}$ und $CeO_{1.88}$ entsprechend dem Zweiphasengebiet $\alpha + \alpha'$, während alle Isothermen oberhalb 700°C in Übereinstimmung mit dem Hochtemperaturröntgenbefund nur einer einzigen homogenen Phase als Bodenkörper entsprechen. Der in der Einleitung genannte Widerspruch zwischen früheren Röntgenbefunden und den Gleichgewichtsmessungen in diesem Bereich erklärt sich nun aus der schon erwähnten raschen Einstellung der Phasengleichgewichte bei Temperaturänderungen. Isothermen bei Temperaturen unter 600°C sind experimentell nicht zugänglich, weil das Redoxgleichgewicht mit der Gasphase sich zu langsam einstellt; eine Isotherme 300°C beispielsweise würde mit ihrem horizontalen Teil die volle Breite der Mischungslücke wiedergeben.

Im Bereich $CeO_{1.81-1.67}$ bestehen bei niederen Temperaturen nach BEVAN mehrere, eng benachbarte rhomboedrische Phasen β, γ und δ sowie die kubische C-Phase. Aus den Hochtemperaturröntgenaufnahmen an dem Präparat $CeO_{1.787}$ sowie den Messungen des Sauerstoffzersetzungsdruckes folgt, dass diese Mannigfaltigkeit sich mit steigender Temperatur sehr stark verringern muss. Alle Redox-Isothermen oberhalb 700°C verlaufen so, dass sie im Bereich $CeO_{1.81}$–$CeO_{1.67}$ nur auf einen einphasigen festen Bodenkörper schliessen lassen. Es ist anzunehmen, dass bei solchen hohen Temperaturen die homogene Reihe der kubischen Mischkristalle sich bis zur Zusammensetzung $CeO_{1.67}$ erstreckt und sich damit dem Verhalten bei analogen heterotypen Systemen wie CeO_2–La_2O_3 anschliesst.

Im Bereich $CeO_{1.67-1.50}$ liegen bei allen Beobachtungstemperaturen zwei koexistierende Phasen vor, wie übereinstimmend aus den Röntgenbefunden und den horizontal verlaufenden Redox-Isothermen hervorgeht. Zu der Frage des Homogenitätsbereiches des hexagonalen Oxyds Ce_2O_3 (A-Typ) können unsere neueren Untersuchungen nichts beitragen.

Die Besonderheit des Verhaltens im System CeO_2–Ce_2O_3 gegenüber den formal völlig entsprechenden Mischsystemen des Cerdioxyds oder Thoriumdioxyds mit den Sesquioxyden der anderen Lanthaniden muss von der Tatsache hergeleitet werden, dass bei den Ceroxyden wegen der Möglichkeit des Elektronenübergangs $Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ die Gitterplätze aller Kationen praktisch gleichwertig sind. Hierauf hat auch BEVAN hingewiesen.[3] Infolge dieser Reaktion brauchen bei Verschiebungen der Grenzzusammensetzung homogener Phasen keine Platzwechselvorgänge der Kationen mit relativ hoher Aktivierungsenergie stattzufinden, sondern nur Elektronensprünge. Hierzu kommen lediglich noch geringfügige geometrische Verschiebungen einzelner Kationen ohne Änderung der Nachbarschaftsverhältnisse beim reversiblen Übergang zwischen der kubischen Struktur und den äusserst nahe verwandten rhomboedrischen Gitterstrukturen. Unsere Untersuchungen scheinen uns diese Auffassung klar zu beweisen. Wir konnten auch durch orientierende Versuche feststellen, dass im analogen Fall von Systemen mit Oxyden zweier verschiedener Metalle bei hoher Temperatur (z.B. 1600°C) eine ausreichende Beweglichkeit der Kationen und relativ rasche Einstellung der Phasengleichgewichte besteht, welche sich aber mit sinkender Temperatur sehr stark verlangsamt. Die Einstelldauer liegt beispielsweise im System ThO_2–Eu_2O_3 für 1600°C in der Grössenordnung von Minuten, für 1300°C jedoch bei ca. 100 Stunden. Bei diesen Oxydsystemen wird man

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also stets nur die stark vereinfachten Hochtemperatur-Phasenverhältnisse ermitteln können, und es besteht wenig Hoffnung die Tieftemperaturverhältnisse zu erfassen, bei denen man eine ähnliche Vielfältigkeit wie bei den Ceroxyden erwarten darf. Die bereits vorliegenden Beobachtungen an den Oxydsystemen PrO_2–Pr_2O_3,[5] TbO_2–Tb_2O_3[6] und UO_3–UO_2[7] lassen erkennen, dass hier die Verhältnisse erwartungsgemäss sehr nahe mit denen beim Ceroxydsystem übereinstimmen.

[5] R. E. Ferguson, E. D. Guth u. L. Eyring, *J. Amer. Chem. Soc.* **76**, 3890 (1954); E. D. Guth, J. R. Holden, N. C. Baenziger u. L. Eyring, *Ibid.* **76**, 5239 (1954); W. Simon u. L. Eyring, *Ibid.* **76**, 5872 (1954); C. L. Sieglaff u. L. Eyring, *Ibid.* **79**, 3024 (1957).
[6] E. D. Guth u. L. Eyring, *J. Amer. Chem. Soc.* **76**, 5242 (1954); W. Simon u. L. Eyring, *Ibid.* **76**, 5872 (1954).
[7] H. Hering u. P. Perio, *Bull. Soc. Chim. Fr.* (5) **19**, 351 (1952); P. Perio, *Ibid.* Mém. (5) **20**, 256 u. 840 (1953); F. Grønvold, *J. Inorg. Nucl. Chem.* **1**, 357 (1955); P. E. Blackburn, *J. Phys. Chem.* **62**, 897 (1958); S. Aronson u. J. Belle, *J. Chem. Phys.* **29**, 151 (1958).

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TOPOTACTICAL REACTIONS WITH FERRIMAGNETIC OXIDES HAVING HEXAGONAL CRYSTAL STRUCTURES—II

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Abstract—A number of reactions between grains of non-oriented and magnetically oriented oxides of the system BaO–MeO–Fe_2O_3 are described. Such conversions, for which the term "topotactical reactions" was introduced in a previous paper, can yield polycrystalline final products with oriented crystals. The reaction mechanism and the influence of sintering on the degree of orientation of the final product is studied for some topotactical reactions.

IN the BaO–MeO-Fe_2O_3 system (Fig. 1), in which Me = Co, Ni, Zn etc., a.o. the ferrimagnetic compounds $M = BaFe_{12}O_{19}$, $Me_2W = BaMe_2Fe_{16}O_{27}$, $Me_2Z = Ba_2Me_2Fe_{24}O_{41}$ and $Me_2Y = Ba_2Me_2Me_2Fe_{12}O_{22}$, having closely related hexagonal

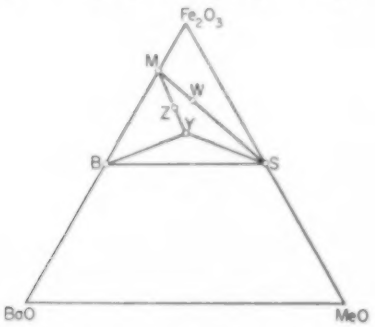

FIG. 1.—Composition diagram of the system BaO–MeO–Fe_2O_3 ($Me^{2+} = Fe^{2+}$, Mn^{2+}, Co^{2+} etc.) $BaFe_{12}O_{19}$(*M*), $Ba_2Me_2Fe_{24}O_{41}$(*Z*), $Ba_2Me_2Fe_{12}O_{22}$(*Y*), $BaMe_2Fe_{16}O_{27}$(*W*), $MeFe_2O_4$(*S*) and $BaFe_2O_4$(*B*).
The compounds $Ba_2Me_2Fe_{28}O_{46}$ and $Ba_4Me_2Fe_{36}O_{60}$, which also exist, will not be mentioned in this paper and are therefore omitted in the diagram.

crystal structures, occur.[1] The grains of these magnetically hard oxides can be oriented by means of a magnetic field. This leads to the possibility of studying crystal orientation phenomena during reactions between oriented and non-oriented grains in mixtures of oxide powders. As described in a previous paper[2] (referred to as paper I) many of such reactions lead to polycrystalline materials with oriented grains. An example of such a "topotactical" reaction is:

$$BaFe_{12}O_{19} \uparrow + 2CoO + 2Fe_2O_3 \rightarrow BaCo_2Fe_{16}O_{27}$$

[1] J. SMIT and H. P. J. WIJN, *Ferrites*. Philips' Technical Library, Eindhoven; John Wiley, New York (1959).
G. H. JONKER, XVI- *Congres international de chimie pure et appliquee*, 1957. Mémoires présentées à la Section de Chimie Minérale, Société d'Editions d'Enseignement Supérieur, Paris, p. 117 (1958).
[2] F. K. LOTGERING, *J. Inorg. Nucl. Chem.* **9**, 113 (1959).

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or $$M \uparrow + 2CoO + 2Fe_2O_3 \rightarrow Co_2W$$

The hexagonal M crystals in the initial mixture are oriented in a magnetic field with their *c*-axes mutually parallel (indicated by the arrow). The reaction takes place by firing the mixture at 1250°C. The final product consists of sintered, polycrystalline Co_2W, the hexagonal crystals of which show the same crystal orientation as the M crystals had in the initial mixture.

A conservation of crystal orientation during a solid state reaction has, as far as we know, never been described in the literature. However, similar, but not exactly the same phenomena, are known. E.g. WESTRIK and ZWIETERING[3] observed that the reduction of a Fe_3O_4 single crystal gives a conglomerate of iron crystals with a preferred orientation. This reaction takes place between a solid and a gas phase and not, as in our case, between solid phases.

The Experimental part of this paper gives

(1) the degree of orientation for a number of reactions between oriented and non-oriented grains,
(2) the analysis of the intermediate reaction products of some of these reactions;
(3) the results of some marker experiments and
(4) experiments concerning the influence of sintering on the crystal orientation.

The experimental results (1) (2) and (3) will be used for the discussion.

EXPERIMENTAL

1. *Degree of orientation*

Table 1 gives the reactions investigated between oriented and non-oriented grains and the degree of crystal orientation of the final products. We refer to paper I for details of the preparation techniques and for the determination of the orientation factor f from the X-ray diffraction pattern of a sample ($f = 0$ and $f = 1$ correspond to no orientation and complete orientation, respectively). For the sake of brevity the equations are formulated with BaO and CoO instead of $BaCO_3$ and $CoCO_3$, which actually were used as raw materials. Further we introduce the symbols *S* for $MeFe_2O_4$ and *B* for $BaFe_2O_4$.

The initial mixtures of the reactions V, VI and X contain $Co_{1/3}Z_{2/3}Z$ as a second ferrimagnetic component. The $Co_{1/3}Zn_{2/3}Z$ crystals, which have a low magnetic anisotropy,[2] are not oriented in a magnetic field so that the initial mixture contains only one oriented crystal phase.

Most of the reactions investigated are conversions of *M*, Me_2W, Me_2Z or Me_2Y into each other so that the crystal structure of the final product is closely related to, or identical with, that of the oriented component in the initial mixture. The question arises whether oriented material can be obtained if this is not the case. We therefore tried to prepare $BaFe_2O_4$, $BaFeO_{3-\delta}$ ($\delta < 0{\cdot}5$) and $TiFe_2O_5$, the crystal structures of which are completely different from those of *M*, Me_2W etc., from the ferrimagnetic hexagonal compounds by the reactions XXI–XXIII. From each of the initial mixtures two pellets were pressed, one in the presence and one in the absence of a magnetic field. The two pellets were fired in the same way. Reactions XXI and XXII occurred as anticipated by the equations. The reaction product of XXIII consisted of the pseudobrookite phase $TiFe_2O_5$ together with a small amount of unidentified material.

A comparison of the X-ray diffraction patterns of the magnetically oriented and the non-oriented pellets did not give any indication for crystal orientation of the $BaFe_2O_4$, $BaFeO_{3-\delta}$ or $TiFe_2O_5$ phases in the oriented samples.

2. *Intermediate reaction products*

For some reactions given in Table 1 the intermediate products that lead from the initial mixture to the final product were investigated in the following way.

A sample was heated up slowly (200–300°C/hr) to a certain temperature (900, 1000, 1100 or

[3] R. WESTRIK and P. ZWIETERING, *Proc. Kon. Ned. Akad. v. Wetenschappen* B **56**, No. 5, 492 (1953).

TABLE 1.—REACTIONS BETWEEN ORIENTED AND NON-ORIENTED GRAINS, THE DENSITY AND CRYSTAL ORIENTATION OF THE FINAL PRODUCTS*

No.	Reaction	Density (g/cm³)	Orientation
I	$\frac{8}{10}M\uparrow + \frac{1}{10}BaO + \frac{1}{10}CoO + \frac{1}{10}TiO_2 \rightarrow BaTi_{1\cdot1}Co_{1\cdot1}Fe_{9\cdot8}O_{19}$	4·5	very good ($f = 0{\cdot}97$)
II	$\frac{1}{2}Co_2Z\perp + \frac{2}{2}BaO + ZnO + 6Fe_2O_3 \rightarrow Co_{1\cdot0}Zn_{1\cdot0}Z$	4·2	good ($f = 0{\cdot}8$)
III	$\frac{1}{2}Zn_2Z\perp + \frac{2}{2}BaO + CoO + 6Fe_2O_3 \rightarrow Co_{1\cdot0}Zn_{1\cdot0}Z$	5·1	good ($f = 0{\cdot}7$)
IV	$\frac{7}{10}Co_2Y\perp$ (35 wt %) + $\frac{13}{10}BaFe_2O_4 + \frac{13}{10}CoO + \frac{13}{10}Fe_2O_3 \rightarrow Co_2Y$	4·4	very good ($f = 0{\cdot}95$)
V	$\frac{1}{2}Co\frac{1}{2}Zn\frac{3}{2}Z$ (33 wt %) + $\frac{2}{2}Co\frac{1}{2}Zn\frac{3}{2}Y\perp$ (36 wt %) + $\frac{2}{2}BaO + 4Fe_2O_3 \rightarrow Co\frac{1}{2}Zn\frac{3}{2}Z$	5·0	non-oriented ($f = 0$)
VI	$\frac{5}{14}Co\frac{4}{4}Zn\frac{3}{4}Y\perp$ (36 wt %) + $\frac{9}{14}Co\frac{1}{4}Zn\frac{3}{4}Z$ (33 wt %) + $\frac{27}{60}BaO + \frac{71}{100}CoO + \frac{31}{100}ZnO + \frac{48}{60}Fe_2O_3 \rightarrow Co\frac{8}{4}Zn\frac{3}{4}Y$	5·0	very good ($f = 0{\cdot}91$)
VII	$M\uparrow + CoO + ZnO + 2Fe_2O_3 \rightarrow Co_{1\cdot0}Zn_{1\cdot0}W$	4·3	very good ($f = 0{\cdot}89$)
VIII	$\frac{1}{2}Zn_2Z\uparrow + CoO + \frac{1}{2}ZnO + 4Fe_2O_3 \rightarrow Co_{1\cdot0}Zn_{1\cdot0}W$	2·8	good ($f = 0{\cdot}84$)
IX	$\frac{1}{2}Co_2Z\uparrow + \frac{1}{15}CoO + \frac{2}{5}ZnO + 4Fe_2O_3 \rightarrow Co_{0\cdot9}Zn_{1\cdot0}W$	3·3	good ($f = 0{\cdot}86$)
X	$\frac{11}{60}M\uparrow$ (15 wt %) + $\frac{13}{60}Co\frac{1}{2}Zn\frac{3}{2}Z$ (42 wt %) + $\frac{17}{25}CoO + \frac{23}{25}Fe_2O_3 \rightarrow Co_{1\cdot01}Zn_{0\cdot29}W$	3·3	good ($f = 0{\cdot}80$)
XI	$Co_2Z\perp + 8Fe_2O_3 \rightarrow 2M + Co_2W$	2·7	M non-oriented Co_2W oriented
XII	$Co_2W\perp + 2BaO + 4Fe_2O_3 \rightarrow Co_2Z$	4·6	good ($f = 0{\cdot}7$)
XIII	$2M\uparrow + BaO + CoO + ZnO \rightarrow Co_{1\cdot0}Zn_{1\cdot0}Z$	4·8	poor ($f = 0{\cdot}1$)
XIV	$Co_2Y\perp + BaO + 6Fe_2O_3 \rightarrow Co_2Z$	4·9	poor ($f = 0{\cdot}1$)
XV	$\frac{3}{4}Co_2W\perp + \frac{1}{4}BaO + \frac{1}{4}CoO \rightarrow Co_2Y$	5·1	good ($f = 0{\cdot}8$)
XVI	$\frac{1}{2}Zn_2Z\uparrow + \frac{1}{2}BaO + ZnO \rightarrow Zn_2Y$	5·1	poor ($f = 0{\cdot}2$)
XVII	$\frac{1}{2}Co_2Z\perp + \frac{1}{2}BaO + CoO \rightarrow Co_2Y$	4·9	good ($f = 0{\cdot}6$)
XVIII	$2Zn_2Z\uparrow + 8ZnO \rightarrow 3Zn_2Y + 6ZnFe_2O_4$	5·2	poor†
XIX	$2Co_2Z\perp + 8CoO \rightarrow 3Co_2Y + 6CoFe_2O_4$	4·8	moderate†
XX	$Co_2Z\perp + BaFe_2O_4 + 5Fe_2O_3 \rightarrow Co_2Z + M$	—	M moderate†
XXI	$\frac{1}{6}M\uparrow + \frac{2}{6}BaO \rightarrow BaFe_2O_4$	—	—
XXII	$\frac{1}{15}M\uparrow + \frac{11}{15}BaO + (\frac{1}{4} - \frac{1}{2}\delta)O_2 \rightarrow BaFeO_{3-\delta}$	—	—
XXIII	$Fe_2^{II}W\uparrow + 10TiO_2 + \frac{1}{2}O_2 \rightarrow 9TiFe_2O_5 + BaTiO_3$	—	—

* The ferrimagnetic grains in the initial mixture were oriented in a static (↑) or rotating (⊥) magnetic field. All samples were fired 3 hr at 1250°C in oxygen. For meaning of symbols M, Me_2W etc. see introduction and Fig. 1.

† f could not be determined with sufficient accuracy for samples with more than one phase.

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1200°C) in oxygen. As soon as the desired temperature was reached, the pellet was quenched and the reaction products were identified by X-ray analysis. The results for four reactions are given in Table 2.

From the phases found at each temperature the partial reactions indicated by arrows in Table 2 can be derived. Since the X-ray reflexions of phases present in small amounts may escape observation, it is not possible to reconstruct the partial reactions in great detail. The principal reactions, however, could be recognized clearly.

TABLE 2.—INTERMEDIATE PRODUCTS OF THE REACTIONS VII, VIII, XII AND XVI, TABLE 1*

Heated up to	Reaction VII $M + CoO + ZnO + 2Fe_2O_3 \rightarrow Co_{1\cdot0}Zn_{1\cdot0}W$	Reaction VIII $\frac{1}{2}Zn_2Z + CoO + \frac{1}{2}ZnO + 4Fe_2O_3 \rightarrow Co_{1\cdot0}Zn_{1\cdot0}W$
	$M + Fe_2O_3 + ZnO + CoO$	$Z + Fe_2O_3 + CoO + ZnO$
900°	$M(s) + Fe_2O_3(w) + S(s)$	$Z(s) + Fe_2O_3(s) + S(s)$
1000°	$M(s) + Fe_2O_3(w) + S(s)$	$Z(s) + Fe_2O_3(s) + S(s)$
1100°	$M(s) + S(s)$	$M(s) + S(s)$
1200°	$M(s) + S(s)$	$M(s) + S(s)$
1250° with annealing	$W(s)$	$W(s)$
	Reaction XII $Co_2W\perp + 2BaO + 4Fe_2O_3 \rightarrow Co_2Z$	Reaction XVI $\frac{1}{2}Zn_2Z\uparrow + \frac{1}{2}BaO + ZnO \rightarrow Zn_2Y$
	$W + BaO + Fe_2O_3$	$Z + BaO + ZnO$
900°	$W(s) + B(s) + Fe_2O_3(m) + S(w) + M(vw)$	$Z(s) + B(s) + ZnO(m)$
1000°	$W(s) + B(s) + Fe_2O_3(m + S(w) + M(vw)$	$Z(s) + B(s) + ZnO(m)$
1100°	$W(s) + B(s) + Y(m) + S(w) + M(m)$	$Z(s) + B(m) + ZnO(m) + Y(s)$
1200°	$W(w) + Y(s) + M(s) + Z(vw)$	$B(vw) + Y(s)$
1250° with annealing	$Z(s)$	$Y(s)$

* The X-ray intensities of the phases are indicated by (*s*) strong; (*m*) moderate; (*w*) weak; (*vw*) very weak.

From Table 2 it is seen that e.g. reaction VII proceeds as follows. ZnO, CoO and Fe_2O_3 react and give a spinel phase *S* at temperatures below 900°C. From 900° to 1200° the reaction product, which exists mainly of *M* and *S*, remains practically unchanged. The final product is formed from *M* and *S* at 1250° after heating for some hours at 1250°C.

3. *Marker experiments*

Two sintered pellets of different compounds were brought into contact. The contact surfaces were ground flat carefully. The boundary was marked by platinum wires (diameter 30 μ) placed in grooves (depth 30 μ) in one of the pellets. The pellets were heated 24 hr at 1250°C and cooled. They could be separated easily and under a stereoscopic microscope it was observed that the position of the wires was unchanged with respect to the boundary. (The error in the estimated position of the wire was much smaller than the diameter of the wire.) X-ray diffraction patterns of the surface layers of the two pellets gave the following results.

In the cases $BaFe_2O_4/Fe_2O_3$, $BaFe_{12}O_{19}/CoFe_2O_4$ and $Ba_2Zn_2Fe_{24}O_{41}/ZnO$ (i.e. reactions of a Ba compound with a compound free from Ba), the reaction products were present exclusively on the pellets of the Ba compound. For the reactions $BaFe_{12}O_{19}/Ba_2Zn_2Fe_{12}O_{22}$ and $BaFe_2O_4/BaCo_2Fe_{16}O_{27}$ (i.e. for which both components contain Ba) the reaction products were found on both pellets.

From these experiments we conclude that the large and heavy Ba^+ ions diffuse much more slowly than the small and light Co^+, Zn^+ and Fe^{2+} ions under circumstances present during topotactical reactions.

4. *The influence of sintering on the degree of orientation*

STUIJTS *et al.*[4] observed on oriented polycrystalline *M* material that the degree of orientation increases with increasing heating time and temperature, which shows that the oriented crystals grow at the expense of the wrongly oriented ones. This was attributed to a lowering of the surface energy. We studied this phenomenon on the following topotactical reactions:

$$x\,Zn_2Z + (1-x)\,Co_2Z \rightarrow Zn_{2x}Co_{2-2x}Z$$

Co_2Z has a preferential plane of magnetization whereas Zn_2Z has a preferential direction and a magnetic anisotropy 4–5 times weaker than that of Co_2Z.[2] In a rotating magnetic field[2] the Co_2Z crystals are oriented with their *c*-axes mutually parallel (the "correct" orientations) whereas the *c*-axes of the Zn_2Z crystals are oriented at random in a plane perpendicular to the *c*-axes of the Co_2Z crystals (the "incorrect" orientations). The "correctly" and "incorrectly" oriented crystals increase and decrease the orientation factor *f*, respectively. Pellets of mixtures with $x = 0$; 0·15; 0·30; 0·50 and 0·70 were pressed in the presence of a rotating field and *f* was determined from the X-ray diagrams. Then the pellets were heated for 16 hr at 1250°C in oxygen, furnace cooled and *f* was determined again. The samples were well sintered and had densities of 5·1–5·2. The *f* vs. *x* curves are given in Fig. 2. For all samples *f* is increased by sintering and the increase is considerable for the higher Zn_2Z contents. Thus the "correctly" oriented crystals are grown at the expense of the "incorrectly" oriented ones by sintering for a long time. Using the same experimental procedure, the increase of *f* during sintering was determined as a function of the sintering time for the mixture $x = 0{\cdot}5$. From the result, given in Table 3, it is seen that the improvement of the orientation increases with increasing density. We therefore think that the improvement of orientation by sintering during a topotactical reaction may be important, but only in the case of a well-sintered final product (with a density of at least 4·5).

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DISCUSSION

We divided the reactions I–XX (Table 1) into four kinds, the prototypes of which are:

(a) $M\uparrow + CoO + ZnO + 2Fe_2O_3 \rightarrow Co_{1\cdot0}Zn_{1\cdot0}W$ (reaction VII)

(b) $\frac{1}{2}Co_2Z\perp + \frac{3}{2}BaO + ZnO + 6Fe_2O_3 \rightarrow Co_{1\cdot0}Zn_{1\cdot0}Z$ (reaction II)

(c) $\frac{7}{10}Co_2Y\perp + \frac{1}{10}\frac{3}{3}B + \frac{1}{10}\frac{3}{3}CoO + \frac{1}{5}\frac{3}{3}Fe_2O_3 \rightarrow Co_2Y$ (reaction IV)

(d) $Co_2Z\perp + B + 5Fe_2O_3 \rightarrow Co_2Z + M$ (reaction XX)

In paper I a topotactical reaction was distinguished from an eptitaxial crystal growth by the fact that the oriented component in the initial mixture, which determines the orientation of the final product, takes part in the reaction and disappears completely. (a) and (b) are covered by this definition of topotactical reaction whereas (c) and (d) are not.

The difference between (a) and (b) is that the crystal structures of the oriented component in the initial mixture and of the final product is equal for (b), but different for (a). During (c) oriented Co_2Y is formed in the presence of oriented Co_2Y crystals i.e. a simple case of crystal growth. In reaction (d) an amount of oriented M is

[4] A. L. STUIJTS, G. W. RATHENAU and G. H. WEBER, *Philips Techn. Rev.* **16**, 141 (1954).

formed in the presence of oriented Co_2Z crystals, which does not take part in the reaction i.e. an epitaxial growth of M on Co_2Z takes place.

1. *Reaction of the types* (b) *and* (c) (I–VI, *Table* 1)

If the initial mixture contains a well oriented phase with the crystal structure of the final product, we found a highly oriented final product in all cases, investigated.

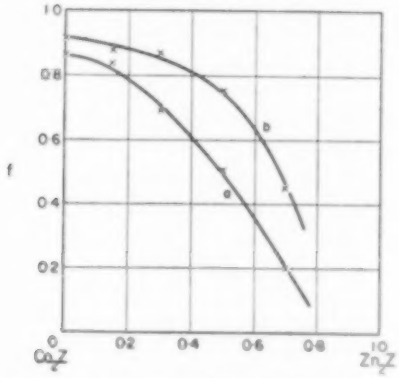

FIG. 2.—Orientation factors f for Co_2Z–Zn_2Z mixtures oriented in a rotating magnetic field. (a) Before firing; (b) after 16 hr firing at 1250°C.

The high degree of orientation of reaction (c) means that the oriented Co_2Y crystal present in the initial mixture act as a substrate for the growth of the Co_2Y produced so that the amount of oriented material increases during the reaction. Apparently practically no new Co_2Y nuclei are formed on the BaO, CoO or Fe_2O_3 crystals (or on their partial reaction products like B or S). This behaviour may be

TABLE 3.—INCREASE OF THE ORIENTATION FACTOR f DURING DIFFERENT HEAT TREATMENTS OF A MIXTURE OF $Co_2Z + Zn_2Z$ (1:1), ORIENTED IN A ROTATING FIELD

Non-fired sample: f_0	Heat treatment: heated up slowly to	fired sample density	fired sample f	$f - f_0$
0·4	1100°C, cooled rapidly	3·4	0·4	0·0
0·3	1250°C, cooled rapidly	4·6	0·5	0·2
0·3	1250°C, ½ hr 1250°C furnace cooled	4·9	0·5	0·2
0·3	1250°C, 3 hr 1250°C furnace cooled	5·0	0·6	0·3
0·5	1250°C, 16 hr 1250°C furnace cooled	5·1	0·7[a]	0·2[a]

connected with the fact that BaO, CoO etc. have crystal structures and compositions completely different from Co_2Y. Then the question arises what happens if the reaction mixture contains two components like Me_2Z and Me_2Y that have closely related crystal structures.

This case was investigated by means of the reactions V and VI. Final product crystals grown on the non-oriented $Co_{1/2}Z_{3/2}Z$ cannot be oriented, whereas the formation of an oriented final product takes place if the oriented $Co_xZn_{2-\delta}Y$ phase acts as a

substrate. Reactions V and VI gave non-oriented and very well oriented final products* respectively. This pronounced difference indicates that the component with the crystal structure of the final product acts preferentially as a substrate for the final product, even if a component with a closely related structure is present in the reaction mixture.

Reaction VI is essentially similar to reaction XVI, both being the formation of Me_2Y from Me_2Z, BaO etc. From the appearance of an Me_2Y phase during reaction XVI after firing for a short time at relatively low temperatures of 1100–1200°C (see Table 2) it is seen that nucleation of Me_2Y takes place easily. It seems to us therefore rather surprising that during reaction VI the segregation of $Co_{5/4}Zn_{3/4}Y$ takes place mainly on the $Co_{3/4}Zn_{3/4}Y$ crystals present in the initial mixture.

The formation of well-oriented final products by topotactical reactions of the type (b) can be easily understood from the above mentioned preference for crystal growth by the assumption that the reaction (b) (or II, Table 1) starts with an epitaxial growth of Zn_2Z on the oriented Co_2Z crystals. Such an eptaxial process differs, however, hardly from crystal growth because the substrate (Co_2Z) and the segregate (Zn_2Z) are practically the same materials (the difference being the kind of Me^{2+} ions, which constitute only 1/13 part of the small cations) A mixed $Co_{1\cdot0}Zn_{1\cdot0}Z$ crystal is then formed by a diffusion of the Co^{2+} and Zn^{2+} ions through a composite grain consisting of Co_2Z and Zn_2Z.

2. *Reactions of the type* (a) (VII–XIX, *Table* 1)

In contrast to the (b)-type, not all (a)-type reactions give well-oriented final products (Table 1). In particular, the reactions XIII, XIV and XVI gave poorly oriented final products. (These reactions we carried out several times. It was verified by X-ray analysis of the unfired pellets that the ferrimagnetic phase in the initial mixtures were indeed well oriented).

During reaction (a) (or VII, Table 1) nucleation of a new phase $Co_{1\cdot0}Zn_{1\cdot0}W$ takes place. The production of highly oriented $Co_{1\cdot0}Zn_{1\cdot0}W$ indicates that the oriented M phase acts mainly as a substrate for the $Co_{1\cdot0}Zn_{1\cdot0}W$ crystals. For the formation of $Co_{1\cdot0}Zn_{1\cdot0}W$ nuclei on M grains a transport of MeO and Fe_2O_3 from the other reaction components toward the M grains is necessary whereas a transport of BaO in the opposite direction must take place for nucleation on the other reaction components, which do not contain Ba. The observed preference for nucleation on the M grains may, therefore, be explained by assuming that the Ba^{2+} ions diffuse much more slowly than the Me^{2+} and Fe^{3+} ions. This assumption was indeed confirmed by the marker experiments (see Experimental Part 3). Not all the experimental data can, however, be explained in this way. The pressence of BaO in the initial mixture should promote the formation of a non-oriented final product. Thus the reactions VII–IX are expected to give better oriented final products than the reactions XII–XVII. Such a tendency is indeed observed. The formation of well-oriented final products by the reactions XII and XV and of a poorly oriented Zn_2Y by reaction XVIII are exceptions, however, for which we are not able to give any explanation.

KEDESDY and DRUKALSKY[5] proposed an atomic mechanism of the formation of a mixed crystal (having NiO-structure) from a NiO and a ZnO crystal. Oxygen atoms diffuse from the ZnO to the

* The high degree of orientation of the final product VI is not caused by sintering (c.f. Experimental Part 4). This was checked by heating the mixture up to 1250°C and cooling the pellet rapidly. The sample was poorly sintered (d = 4·3) and still very well oriented (f = 0.92).

[5] H. KEDESDY and A. DRUKALSKY, *J. Amer. Chem. Soc.* **76**, 5941 (1954).

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NiO crystal and build up a new oxygen layer on the NiO surface. Then a diffusion of Zn atoms from the ZnO into the NiO crystal follows. According to this picture the oxygen "frame" of the NiO lattice remains intact and increases layer for layer during the reaction. This process would lead to a topotactically oriented mixed crystal with the orientation of the original NiO crystal.

A similar mechanism for e.g. the formation of a Me_2W nucleus on a M crystal (reaction VII) would explain nicely the orientation of the Me_2W crystal. Such a mechanism, which seems to us quite possible in the case of the mixed NiO–ZnO crystal, is, however, very unlikely for our much more complicated reaction. Although the crystal structures of Me_2W and M are closely related, the oxygen frame and the positions of the Ba^{+} ions in this frame are different for both structures. For a transition of the M into the Me_2W lattice a rearrangenemt of the O^{2-} and Ba^{2+} is necessary. It is hard to believe that during such a process parts of the oxygen frame remain intact. It seems to us much more likely that the topotactical reaction VII starts with an epitaxial growth of Me_2W crystals on the surfaces of the M crystals.

The spacings of the oxygen layers of M, Me_2W, Me_2Z and Me_2Y are practically equal and parts of these lattices have even the same atomic arrangement (e.g. the M and Me_2W lattices contain layers having spinel structure with an identical atomic arrangement. The only difference is that the cation sites are occupied by Fe^{3+} in M and by Fe^{3+} and Me^{2+} in Me_2W). Therefore the conditions for an epitaxial growth for M, Me_2W etc. (and S) on each other are expected to be very favourable. Such an epitaxial growth is observed during reaction XX.

3. *Intermediate products* (*Table* 2)

A topotactical reaction leads to the final product via several intermediate products which appear during the heat treatment of the pellet. $B = BaFe_2O_4$ and $S = MeFe_2O_4$ are formed at relatively low temperatures (below 900°C). At a higher temperature (1000–1100°C) M and Me_2Y appear. The final products Me_2W and Me_2Z are generally formed only after a longer firing at a still higher temperature (1250°C) by the reactions:

$$M + 2S \rightarrow Me_2W \text{ and } M + Me_2Y \rightarrow Me_2Z$$

During reaction VIII a double conversion from Zn_2Z and Fe_2O_3 into M and S takes place between 1000 and 1100°C. Since the Zn_2Z crystals, which were oriented in the magnetic field, have disappeared at temperatures above 1100°C and well-oriented Me_2W does not start to appear until 1250°C is reached, the conservation of the orientation must take place via the M phase.

Reaction X (Table 1) gives a well-oriented final product although the initial mixture contains only a small amount (15 weight per cent) of the oriented component M and a large amount (42 weight per cent) of non-oriented $Co_{1/2}Zn_{3/2}Z$. The presence of the latter component evidently causes no formation of a considerable amount of non-oriented final product. This may be explained as follows. From an analysis of the intermediate reaction products it was found that a double conversion $Me_2Z + 8Fe_2O_3 \rightarrow 3M + 2MeFe_2O_4$ at temperatures between 1000 and 1100°C occurs here also, just as during reaction VIII. The large amount of M formed in this way will grow on the oriented M crystals present in the initial mixture (reaction of type (c)). Then, at 1250°C, well-oriented Me_2W is formed from the oriented M phase and S, just like during the reactions VII and VIII.

In connexion with the above-mentioned mechanism of the reactions VIII–X we investigated the conversion of Co_2Z and Fe_2O_3 into M and Co_2W (reaction XI, Table 1). The final product consists of non-oriented M and oriented Co_2W. From an analysis of the intermediate reaction products it was found that the reaction takes place as given by equation XI at temperatures between 1000 and 1100°C and that no spinel phase appears during the reaction. Thus the double conversion

XI differs from the double conversions that take place during the reactions VIII–X in the orientations of *M* and *W*; the reaction mechanism is also different. This difference of mechanism may be caused by the fact that the double conversions during the reactions VIII-X proceed in the presence of a *S* phase (Table 2), which may promote further *S* formation, whereas no *S* phase is present when reaction XI starts.

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ADSORPTION OF COBALT, ZINC, BARIUM AND CESIUM FROM DILUTE SOLUTIONS

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Abstract—It has been shown that a maximum of 97 per cent of the zinc in a solution containing 8×10^{-8} mole/30 ml can be removed from solution by a single filtration through Schleicher and Schuell Blue Ribbon paper at pH 6·5 when the ammonium salt concentration is 3×10^{-6} M. Under similar conditions 70 per cent of the cobalt present in a solution containing $2{\cdot}8 \times 10^{-9}$ mole/30 ml can be removed. Only 43–46 per cent of barium and 5–6 per cent of cesium are removed from solutions which have 3×10^{-9} mole/30 ml and less than 10^{-8} mole/30ml respectively. The above results permit the conclusion that unweighable quantities of zinc and cobalt ions in solution with cesium, and probably other alkali metal salts can be separated from these salts by adjustment of pH with ammonia and filtering the solutions. The cobalt and zinc which may be radioactive are recoverable in almost invisible quantities of solid, (after ammonium salt sublimation) suitable for nuclear spectroscopy studies or for other use which requires relatively salt free high specific activity tracers.

THIS work is a study of the behaviour of zinc and cobalt in microgramme quantities (or less), as they are obtained in activated targets, and a comparison of their behaviour with that of barium and cesium from the point of view of possible separations of the alkali and alkaline earth elements (frequent contaminants in target work) from zinc and cobalt.

The tendency of some elements in a very low concentration to be removed from solution by filtration through paper has been utilized in a variety of separations[1] of tetra- and tri-valent ions from each other and from divalent ions. However, as yet, little is known concerning the possibility of isolating divalent elements from activated targets by this method nor has the method been used to separate divalent transition elements from alkali and alkaline earth ions.

This research consists of determinations of the extent to which paper filtration removes cobalt, zinc, barium and cesium from dilute solutions under similar conditions and the optimum conditions for such removal. The value of the process lies in its simplicity and the rapidity of separation of unweighable quantities of radioactive species from weighable amounts of target material.

EXPERIMENTAL

Cobalt-60, $T_{1/2} = 5{\cdot}3$ years, was obtained by neutron irradiation of a cobalt wire to high specific activity at the Oak Ridge National Laboratories. Zinc-60, $T_{1/2} = 250$ days, was obtained likewise by neutron irradiation of metallic zinc in the pile at Oak Ridge National Laboratories. Barium-133, $T_{1/2} = 38{\cdot}8$ hr, was produced by cyclotron bombardment of a cesium chloride target with deuterons. The barium was removed from the cesium by adsorption on hydrous ferric oxide. Barium-131 was produced by neutron irradiation of barium nitrate at Oak Ridge. This decays by *K*-capture to cesium-131, $T_{1/2} = 10{\cdot}2$ days, which was separated from the barium.

[1] M. H. KURBATOV, H. B. WEBSTER, J. D. KURBATOV, *J. Phys. Colloid Chem.* **54**, 1239 (1950); J. E. DUVAL and M. H. KURBATOV, *J. Amer. Chem. Soc.* **75**, 2246 (1953); J. D. KURBATOV and M. H. KURBATOV, *J. Phys. Chem.* **46**, 441 (1942); M. H. KURBATOV and J. D. KURBATOV, *J. Chem. Phys.* **13**, 208 (1945).

Throughout this work the volumes of solution, which contained the radioactive material to be studied, were such that after titration to various pH values the final volume was 30·0 ± 0·2 ml. The temperature was 27 ± 1°. Except in those cases indicated later the solutions were filtered, within 15 min after titration, through Schleicher and Schuell Blue Ribbon paper. The material which was retained by the paper was removed into sample holders by washing the paper with hot six-normal hydrochloric acid. The samples were evaporated to dryness, and the amount of activity present measured by use of a Geiger counter.

RESULTS AND DISCUSSION

As background data for studies of low concentrations of zinc and cobalt, isotherms for their removal from solutions of various concentrations were obtained at pH 6·5. Column A of Table 1 has the zinc isotherm data. It may be seen that the fraction removed by paper drops off rapidly from 97 per cent at 8×10^{-8} mole zinc per 30 ml to 7 per cent at 1×10^{-4} mole. These data were obtained by preparing solutions of zinc chloride of different concentrations and titrating to pH 6·5 with ammonia. As a result of hydrolysis the solutions of higher concentrations of zinc were more acidic, than the lower concentrations, and at pH 6·5 contained more ammonium salt.

TABLE 1.—EFFECT OF CONCENTRATION OF SOLUTIONS ON REMOVAL OF Zn AND Co BY FILTRATION AT pH 6·5

Quantity of divalent cation (mole/30 ml)	A* Zn on paper (%)	B* Co on paper (%)
$1{\cdot}4 \times 10^{-9}$		60
1×10^{-8}		56
8×10^{-8}	97	
1×10^{-7}		47
$1{\cdot}8 \times 10^{-7}$	89	
2×10^{-7}		39
$2{\cdot}8 \times 10^{-7}$	71	
5×10^{-7}		
$5{\cdot}8 \times 10^{-7}$	56	
1×10^{-6}	32	23
2×10^{-6}		15·4
1×10^{-5}	7·8	5·6
1×10^{-4}	6·8	1·6
1×10^{-3}		1·5

* A: Zn isotherm, 448 counts/min of active Zn per 30 ml. B: Co isotherm, 1305 counts/min of active Co per 30 ml.

The cobalt isotherm data, Column B, Table 1 were obtained on solutions to which 2×10^{-5} mole of hydrochloric acid was added in order to maintain a constant ammonium salt concentration in solutions having less than 1×10^{-5} of cobalt chloride. The fraction of cobalt retained by the paper is much lower, in the low concentration region than the fraction of zinc retained.

The effect of ammonium salts was studied by varying the concentrations of ammonium chloride and sulphate in the presence of a constant concentration of zinc ($8{\cdot}2 \times 10^{-8}$ mole/30 ml). The results showed that an increase in chloride ion concentration from 1×10^{-6} to 1×10^{-3} equivalents per 30 ml decreased the amount of zinc

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retained on the paper from 92 to 8 per cent. Similarly a change in sulphate ion concentration from 2×10^{-7} to 2×10^{-3} equivalents per 30 ml decreased the zinc adsorption from 95 to 7 per cent. At low concentrations of salt slightly more (between 2 and 5 per cent) zinc is retained by the paper in the presence of sulphate ion than with chloride ion.

In all of this work it was observed that some of the zinc or cobalt was adsorbed on the surface of the beaker in which the solutions were titrated. The amount of this adsorption was found to vary in an irregular fashion from less than 1 per cent to as much as 6 or 7 per cent. When solutions which contained $2{\cdot}8 \times 10^{-9}$ mole of cobalt per 30 ml were allowed to stand in glass for three days after titration to various pH values there was an increase in the amount adsorbed with increasing basicity, from 0·2 per cent at pH 3·66 to 54 per cent at pH 9·72.

Because of the discussion in the literature concerning "radiocolloid" adsorption (or filtration) vs adsorption of ions a series of experiments was carried out in which the solutions were titrated to a given pH, allowed to stand for three days and then filtered through two papers in separate funnels; one placed just below the other. If preformed agglomerates were present and removed by the paper and if these agglomerates require more time for their formation than the minute or less elapsed time between successive filtrations of a given portion of solution then the first paper should retain a higher fraction of the cobalt which came in contact with it than the second paper. The data show that this is not the case and that the fraction removed on the second paper is usually higher. This higher fraction on the second paper is in accord with the trend shown in the isotherm, that is, a greater fraction is adsorbed at lower concentrations for a given pH.

Since cobalt and zinc form ammonia complexes, in the study of the effect of pH upon their removal from solution by filtration, one series of experiments with cobalt was run with sodium hydroxide as the base whereas ammonia solution was used in the others. The results so obtained are plotted in Fig. 1, Curve B' for contrast with Curve B which is a plot of the data obtained with ammonia.

It is apparent from Fig. 1 that the data on the effect of pH and/or ammonia concentration, on the paper removal of the above ions from solution, falls into three regions. From pH 3·5 to about 6·5 there is a regular increase in removal with increase in pH for zinc, cobalt and barium. For cobalt solutions the figures obtained with sodium hydroxide and ammonium hydroxide give essentially the same curve in this pH range. JOHN[2] has shown that the zeta-potential of Schleicher and Schuell Blue Ribbon paper (in lithium chloride solutions) changes from 0 at pH 3·0 to $-1{\cdot}46$ at pH 4·0 to $-2{\cdot}2$ at pH 6·5 and thereafter remains essentially constant at $-2{\cdot}2$ up to pH 9. It appears then that the nearly constant slope of the four curves in the pH range from 3·5 to 6·5 is primarily a function of the changing charge on the paper.

In the study of the effect of pH at constant salt concentration the maximum fraction of ions removed were: 86 per cent of the zinc, 70 per cent of the cobalt and 46 per cent of the barium. These figures parallel the solubilities of the hydroxides although the concentrations of zinc, cobalt and barium were below those of saturated solutions of their hydroxides. It may be noted that the fraction of zinc removed by paper in the study of pH effect is less than that shown in Table 1, the difference resulting from a higher concentration of salt in the experiments on the effect of pH. The maximum

[2] G. JOHN, Ph.D. Dissertation, The Ohio State University (1952).

cobalt removal here is higher than in Table 1, the salt concentration being lower in these experiments on effect of pH.

Between pH 6·5 and 9 there is a marked contrast in the four curves in Fig. 1. Curve *B′* which represents data obtained with cobalt solutions titrated with sodium hydroxide and Curve *C*, barium solutions titrated with ammonia solution are, within experimental error, horizontal lines in this pH range. The actual figures for cobalt removal on paper were 68, 71 and 69 per cent adsorbed and for barium the figures ranged from 43 to 46 per cent. The curves *A* and *B*, for zinc and cobalt titrated with ammonia solution, drop in approximately parallel fashion between pH 6·5 and 9. An apparent

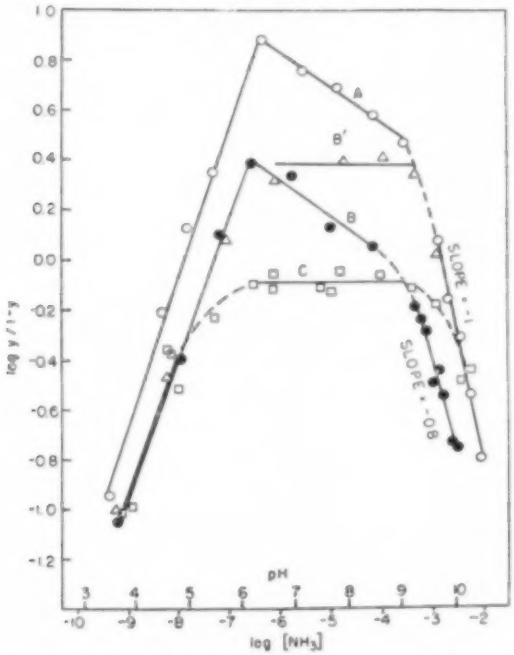

FIG. 1.—Paper filtration curves: *A*, zinc chloride solution, $8{\cdot}2 \times 10^{-6}$ mole/30 ml, titrated with ammonia; *B*, cobalt chloride solution, $2{\cdot}8 \times 10^{-6}$ mole/30 ml, titrated with ammonia; *B′*, same as *B* except solution titrated with NaOH: *C*, barium chloride solution, $2{\cdot}8 \times 10^{-9}$ mole/30 ml. All solutions contained 1×10^{-5} mole HCl before titration. The ratio of the fraction adsorbed to the fraction in solution is given as $Y/1 - Y$.

reason for the difference between these two curves and the two curves mentioned above is that zinc and cobalt form ammonia complexes in the pH range from 6·5 to 9.

At about pH 9 all of the curves turn down. The change in direction of the curve may be attributed in large part to hydrolysis of zinc and cobalt to ions of lower charge. The fact that the barium curve drops too may represent a change in charge or structure of the paper in alkaline solution and this would, of course, be an additional factor in the case of the zinc and cobalt behaviour.

SCHWEITZER and JACKSON[3] have reported 66–69 per cent removal of calcium on paper between pH 10 and 12.

Similar data to the above were obtained for cesium. Between 5 and 6 per cent of

[3] G. K. SCHWEITZER and W. M. JACKSON, *J. Amer. Chem. Soc.* **76**, 941 (1954).

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the cesium was removed between pH 6 and 9. SCHWEITZER and JACKSON[3] have reported "erratic" sodium and cesium removal from solution on paper from 7 to 14 per cent and 9 to 17 per cent respectively in the pH range of 0 to 10.

An interesting comparison can be made between the behaviour of zinc upon filtration, as described here, and the observations of SCHWEITZER and BISHOP[4] on the extent to which zinc can be removed from solution by centrifuging. Their curve is of similar shape but is displaced approximately two and a half pH units higher than the filtration curve presented here.

In conclusion it may be said that solutions of active zinc and cobalt in concentrations as low as 10^{-6} and 10^{-7} mole/l. can be freed of cesium and probably some other alkali ions by adjustment of pH with ammonia to approximately 6·5, filtration or repeated filtration of the solution and recovery of the active cobalt or zinc from the paper by dissolving in hydrochloric acid. The whole procedure requires about a half hour and the product is one contaminated only by small quantities of the readily removed ammonium salts.

This process has been used in subsequent work[5] to remove zinc-65, copper-64 and potassium-42 from rhodium by first adsorbing the zinc and copper from a solution of potassium-42 and rhodium (in the form of a chloride complex) and then adsorbing rhodium cations leaving potassium in solution.

Acknowledgement—The authors gratefully acknowledge their indebtedness to the Ohio State University Research Foundation and to The U.S. Atomic Energy Commission, Contract No. AT(11-1)-469, under the auspices of which this work was done.

[4] G. K. SCHWEITZER and W. N. BISHOP, *J. Amer. Chem. Soc.* **76**, 4321 (1954).
[5] M. H. KURBATOV and C. W. TOWNLEY, *J. Inorg. Nucl. Chem.* In press.

J. Inorg. Nucl. Chem., 1960, Vol. 16, pp. 114 to 123. Pergamon Press Ltd. Printed in Northern Ireland

A STUDY OF TRANSFERENCE AND SOLVATION PHENOMENA—II

SILVER PERCHLORATE IN WATER, WATER–ETHANOL, AND ETHANOL SOLVENTS

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Abstract—For water solvent the transference number of silver ion in silver perchlorate decreases slowly but linearly with decreasing concentration of the salt and extrapolates to 0·488 ± 0·005 at infinite dilution. This value agrees quite well with values for dilute solutions recorded in the literature. The moles of water carried per mole of cation increases with decreasing weight per cent silver perchlorate as is to be expected and is in agreement with the decrease of the transference number with increasing weight per cent ethanol.

There was first a small linear decrease of transference number of the silver ion with increasing weight per cent ethanol out to about fifty-five weight per cent ethanol. Then there is an accelerated rate of decrease of the transference number up to about eighty-five weight per cent ethanol when the rate of decrease again decelerates.

The solvation data indicate that silver ion carries an excess of water compared to the perchlorate ion while the perchlorate ion seems to carry alcohol molecules in an amount equal to or greater than the silver ion depending on how the basis of comparison is determined. These data might be interpreted as showing selective solvation of silver and perchlorate ions by water and ethanol, respectively.

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INTERESTING transport and solvation phenomena were found in a study of the ions of uranyl chloride in water, water–ethanol, and ethanol solvents.[1] As a part of a general program of the study of transference and solvation of ions in solution, silver perchlorate was chosen as a promising salt to investigate since the perchlorate ion would perhaps show less tendency to form complexes than other anions, and thus the ions from silver perchlorate would perhaps be as elementary as from any other salt one could choose.

EXPERIMENTAL

Anhydrous silver perchlorate, reagent grade, was purchased from G. Frederick Smith Chemical Company. Raffinose was obtained from Eastman Organic Chemicals, and α-methyl-D-glucoside from Nutritional Biochemicals. The silver wire and all other chemicals used were reagent quality.

In solvents of 85·8 and greater weight per cent ethanol, α-methyl-D-glucoside was used instead of raffinose as the inert substance for solvation determinations. This was necessary since raffinose was not soluble enough in the high weight per cent ethanol solvents to give sufficient rotation for accurate measurements. The α-methyl- rather than the α-ethyl-D-glucoside was used since the ethyl compound was not commercially available in a sufficient state of purity.

Weights were calibrated against U.S. Bureau of Standards weights and the thermometer against a U.S. Bureau of Standards thermometer.

The transference cell, cell support, coulometers, sodium lamp, pycnometers and constant temperature bath were similar to those described by MATHEWS *et al.*[1]

In water the solutions were prepared by dissolving the desired amount of silver perchlorate and, if the solvation number was to be determined, about 40 g of raffinose in about 600 ml of distilled

[1] D. M. MATHEWS, J. O. WEAR and E. S. AMIS, *J. Inorg. Nucl. Chem.* **13**, 298 (1960).

water. The silver perchlorate as purchased contained traces of silver chloride. Therefore the solution was filtered through a fine glass frit into a 1000 ml volumetric flask. Washings from the containing vessel and frit were also caught in the flask and the whole diluted to the mark.

The clean cell was rinsed once with about 100 ml of solution to be used; this solution was discarded and the cell filled with another portion of solution. This portion was poured back into the main portion of the solution and the sell refilled. Special care was taken to see that there were no air bubbles around the electrodes so that the formation of any gas during the transference experiment could be detected. The cell and contents were placed in the thermostatic bath at 25·00 ± 0·05° and allowed to come to temperature equilibrium before the current was started.

A current of 25 mA was passed through the solution for about 10 hr. The care exercised by MATHEWS *et al.*[1] was observed during all transference runs to prevent vibrations which would have disturbed the solution in the cell.

At the end of the run the stopcocks were carefully closed so as to isolate the various compartments. The solutions from the compartments were transferred to separate ground-glass-stoppered Erlenmeyer flasks. The flasks used for the anode and cathode compartments were previously tared. The solutions remaining in the anode and cathode compartments (on the walls and electrodes) were quantitatively washed into separate beakers and the total silver content of each determined. From the total silver remaining in each compartment and the grammes of silver per gramme of undiluted solution from the compartment, the weight of solution that remained in the compartment could be calculated. Thus after weighing the tared flasks containing the solutions and analysing the solutions, the total weight of solution in each compartment was obtained.

The weights of silver deposited in the caulometers were determined as described by MATHEWS *et al.*[1]

Clean, dry weight burettes were rinsed three times with the solution to be analysed. Into these were placed solutions taken from each compartment and the original solution. Three samples were weighed from each burette. These samples were analysed for silver by precipitation as silver chloride using a standard procedure.[2] If the original solution and the solution from the middle compartment differed appreciably in concentration, the transference run was abandoned.

The transference number of silver was calculated using the weights of the solutions and the concentrations of silver in the various compartments, and the weight of silver deposited in the coulommeters.

If solvation numbers were to be determined also, the angles of rotation of the various solutions were determined at 25·00 ± 0·05° as described in ref. 1.

In water–alcohol and almost pure alcohol solutions, gas was generated at the anode. For this reason the anode was vented through a glass tube to the atmosphere; and only the cathode compartment could be used to determine transference and solvation numbers. Hence, 2 l. of solution were made for these runs which were made in duplicate for the purpose of checking results. In 30 and 60 weight per cent ethanol solvents, 2 weight per cent raffinose was used as the inert reference substance. In solutions containing 85 and greater weight per cent ethanol 1·7 weight per cent α-methyl-D-glucoside served as the inert reference substance.

The ethanol concentrations in the solvent were determined from density measurements using the data of OSBORNE *et al.*[3] as reference.

TREATMENT OF DATA

WASHBURN[4] has proposed a simple formula for calculating Hittorf transference numbers, namely

$$N_F - N_0 = N_E - N_B t \tag{1}$$

or

$$t = \frac{N_0 - N_F + N_E}{N_B} \tag{2}$$

where N_0 and N_F represent the original and final number of equivalents of an ion associated with a

[1] W. C. PIERCE, E. L. HAENISCH and D. L. SAWYER, *Quantitative Analysis* pp. 357–360. John Wiley, New York (1958).
[2] N. S. OSBORNE, E. C. MCKELVY and H. W. BEARCE, *Bull. Bur. Stand.* **9**, 424 (1913).
[3] E. W. WASHBURN, *Principles of Physical Chemistry* p. 276. McGraw-Hill, New York (1921).

given weight of solvent, N_E is the number of equivalents of this ion added to this weight of solvent by the electrode reaction, and t is the transference number of the ion.

Other symbols used in this discussion are defined as follows:

P_s^a = grammes of silver perchlorate per 100 g of anode portion.
P_s^m = grammes of silver perchlorate per 100 g of middle portion.
P_s^c = grammes of silver perchlorate per 100 grammes of cathode portion.
w^a = weight of anode solution in grammes.
w^c = weight of cathode solution in grammes.
w = weight of silver deposited in the coulometer.
20734 = 100 × molecular weight of silver perchlorate.
t_c = Hittorf transference number of the cation.
t_a = Hittorf transference number of the anion.
N_S^a = number of equivalents of cation associated with the weight of the solvent in the anode compartment finally.
N_o^a = number of equivalents of cation originally associated with a like amount of solvent.
f_s^m = fraction of the middle compartment solution that is salt.
f_s^a = fraction of the anode compartment solution that is salt.
$[\alpha]_D^t$ = specific rotation of the inert solute for the yellow D-line of sodium at 25°.
α_m = measured rotation of the solution from the middle portion.
α_a = measured rotation of the solution from the anode compartment.
d_m = density of the solution from the middle compartment.
d_a = density of the solution from the anode compartment.
4 = length of the polarimeter tube in decimeters.
g_m = grammes of inert reference substance per 100 g of solution from the middle compartment other than salt.
g_a = grammes of inert reference substance per 100 g of solution from the anode compartment other than salt.
ΔG_a^E = grammes of solvent transferred per faraday from the anode compartment.
ΔG_c^E = grammes of solvent transferred per faraday to the cathode compartment.
ΔN_a^E = moles of solvent transferred per faraday from the anode compartment.
ΔN_c^E = moles of solvent transferred per faraday to the cathode compartment.
F = the faraday.
M = molecular weight of the solvent.
T_c = true transference number of the cation.
N_c = number of moles of solvent per mole of cation.
N_a = number of moles of solvent per mole of anion.

From Washburn's equation, the transference number of the cation is

$$t_c = 1 - \frac{N_S^a - N_O^a}{N_E} \tag{3}$$

Now

$$N_S^a = \frac{P_s^a\, w^a}{20734} \tag{4}$$

$$N_O^a = \frac{P_s^m w^a (100 - P_s^a)}{20734(100 - P_s^m)} \tag{5}$$

and

$$N_E = \frac{w}{107{\cdot}88} \tag{6}$$

Substituting N_S^a, N_O^a and N_E from equations (4), (5) and (6) into equation (3) gives

$$t_c = 1 - \left(\frac{P_s^a}{100 - P_s^a} - \frac{P_s^m}{100 - P_s^m}\right)\frac{w^a(100 - P_s^a)0{\cdot}052030}{w} \tag{7}$$

A similar equation can be derived for the transference number of the anion using the data from

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the cathode compartment. The equation is

$$t_a = \left(\frac{P_s^m}{100 - P_s^m} - \frac{P_s^c}{100 - P_s^c}\right)\frac{w^c(100 - P_s^c)0{\cdot}052030}{w} \tag{8}$$

Of course an equation for t_a can be found by subtracting the value of t_c from unity and an equation for t_c by subtracting the value of t_a from unity.

Following a procedure similar to that of MATHEWS *et al.*[1] an equation can be derived for the difference in grammes of optically active material per 100 g of solution in the anode compartment as compared to the middle compartment, when the measured rotations of the solutions from the two compartments are corrected to equal weight fractions of salt in the solutions. The equation is:

$$g_a - g_m = \frac{100}{4[\alpha]_D^t} \cdot \left[\frac{\alpha_a(1 - f_s^m)}{d_a(1 - f_s^a)} - \frac{\alpha_m}{d_m}\right] \tag{9}$$

This equation multiplied by $w_a/100$, the weight of the anode compartment in hundreds of grammes gives the total difference in weight of inert substance between the middle and anode compartments. This change in grammes of inert substance divided by grammes of inert substance per gram of solution gives the grammes of solution to contain this weight of inert substance, and this is the weight of solution that must be replaced by solvent in order to cause the measured difference in the concentration of inert substance. Again following the procedure of MATHEWS *et al.*[1] the grammes of solvent transferred away from the anode compartment per faraday are

$$\Delta G_a^F = \left[\alpha_a \frac{(1 - f_s^m)}{(1 - f_s^a)} - \frac{\alpha_m d_a}{d_m}\right]\frac{w^a}{\alpha_a} \tag{10}$$

and the moles of solvent transported per faraday from the anode compartment are

$$\Delta N_a^F = \left[\alpha_a \frac{(1 - f_s^m)}{(1 - f_s^a)} - \alpha_m \frac{d_a}{d_m}\right]\frac{w^a}{MF\alpha_a} = \left[\alpha_a \frac{(100 - P_s^m)}{(100 - P_s^a)} - \alpha_m \frac{d_a}{d_m}\right]\frac{w^a}{MF\alpha_a} \tag{11}$$

Similarly the moles of solvent transported per faraday to the cathode compartment are:

$$\Delta N_c^F = \left[\alpha_m \frac{(1 - f_s^c)}{(1 - f_s^m)} - \alpha_c \frac{d_m}{d_c}\right]\frac{w_c}{MF\alpha_m} = \left[\alpha_m \frac{(100 - P_s^c)}{(100 - P_s^m)} - \alpha_c \frac{d_m}{d_c}\right]\frac{w^c}{MF\alpha_m} \tag{12}$$

In these derivations it has been assumed that the density of the solvent that replaces the solution is the same as that of the solution.

DATA AND DISCUSSION

In Table 1 are listed the Hittorf transference number of the cation, t_c, and the moles of water, N_c, per mole of cation at 25° for various concentrations of silver perchlorate. From the plot of the transference number of the cation vs. weight per cent silver perchlorate in Fig. 1, one can see that the transference number of silver ion in the salt slowly decreases with decreasing concentration of the silver perchlorate and extrapolates to 0·488 ± 0·005 at infinite dilution. This is in good agreement with the value 0·486 given by LOEB and NERNST[5] for 0·0245 M (approximately 0·5 weight per cent) silver perchlorate at 25°. MACINNES, *et al.*[6] give 61·92 cm² V⁻¹ sec⁻¹ as the limiting ionic mobility of the silver ion, and JONES[7] gives 67·32 cm² V⁻¹ sec⁻¹ as that of the perchlorate ion. From these limiting mobilities, the transference number at infinite dilution of the silver ion calculates to be 0·479 in good agreement with the value 0·488 ± 0·005. From Table 1 it is also evident that the

[5] M. LOEB and W. NERNST, *Z. Phys. Chem.* **2**, 948 (1888).
[6] D. A. MACINNES, T. SHEDLOVSKY and L. G. LONGSWORTH, *J. Amer. Chem. Soc.* **54**, 2758 (1932).
[7] J. H. JONES, *J. Amer. Chem. Soc.* **67**, 855 (1945).

Table 1.—Hittorf transference number of the cation, t_c and moles of water of solvation per mole of ion at different concentrations of silver perchlorate in water at 25°C

	P_s^m	P_s^a, P_s^c	w^a, w^c	w	t_c	α_m	α_a, α_c	d_m	d_a, d_d	ΔN_w^f	N_c	T_c
1. Anode	1·9014	1·3060	177·34	1·1755	0·481							
2. Anode	3·625	4·217	161·10	1·0228	0·497	18·6388	18·6908	1·0421	1·0445	5·05	10·04	0·503
3. Anode	3·872	4·581	168·69	1·2639	0·488							
4. Cathode	7·175	6·645	168·71	·9866	0·492	18·319	18·260	1·0699	1·0653	4·64	9·34	0·497
5. Anode	7·186	7·730	166·69	1·0899	0·511							
6. Cathode	7·294	6·580	167·24	1·2536	0·499							
7. Anode	8·610	9·170	163·63	1·0504	0·503	12·9040	12·9490	1·0810	1·0862	4·52	8·32	0·507
8. Cathode	8·610	8·076	171·38	1·0504	0·504	12·9040	12·8431	1·0810	1·0747	4·62	9·09	0·508
9. Anode	10·632	11·145	178·49	1·1008	0·511							
10. Anode	10·645	11·128	175·86	1·0009	0·506							
11. Cathode	13·912	13·422	187·31	1·0700	0·518							
12. Anode	19·707	20·172	192·36	1·1225	0·526							
13. Cathode	19·707	19·223	182·54	1·1225	0·532							

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transference numbers are in fair agreement whether the data were taken using the anode or using the cathode compartment. Rows 4, 5, and 6 illustrate this observation for independent runs and rows 7 and 8, and 12 and 13 show the agreement for data taken in the same experiment. There is a tendency for the cathode to give slightly higher values for the transference number of the silver ion.

STEEL and STOKES[8] and STEEL *et al.*[9] using a conductance technique to ascertain the concentrations of the electrolytes calculated no single determinate error was greater than 0·1 per cent for Hittorf transference numbers in relatively dilute solutions

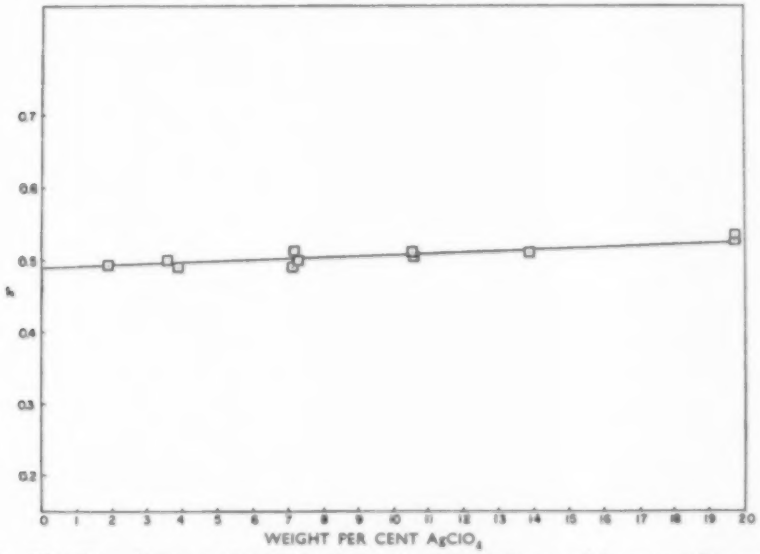

FIG. 1.—Hittorf transference number of the cation, t_+, in water solution vs. weight per cent silver perchlorate.

of salts in water–sucrose and water–glycerol solvents. By their method solvation numbers of the ions were not found. The method involves some doubtful elements but checks closely values found for transference numbers using the moving boundary method. Their data for the mobility of Ag^+ and ClO_4^- ions in 10 and 20 per cent by weight sucrose in water involve the same number of significant figures as our data on transference numbers. The values of the transference numbers of silver ion calculated from the mobilities of Ag^+ and ClO_4^- ions in 10 and 20 per cent by weight sucrose solvents were 0·478 and 0·477, respectively. These values compare favourably with the values 0·477 and 0·476 reported in this paper for 10 and 20 per cent by weight ethanol solvents (see Fig. 3).

Fig. 1 shows the dependence of transference number on concentration to be linear. Theoretically the transference number of an ion from a uni-univalent electrolyte should in the limit of infinite dilution be a linear function of the square root of the concentration.[10]

From Fig. 2 it is seen that the moles of water carried per mole of cation decreases with increasing weight per cent silver perchlorate. This trend is opposite to that for

[8] B. J. STEEL and R. H. STOKES, *J. Phys. Chem.* **62**, 450 (1958).
[9] B. J. STEEL, J. M. STOKES and R. H. STOKES, *J. Phys. Chem.* **62**, 1514 (1958).
[10] D. A. MACINNES, *The Principles of Electrochemistry* pp. 331–334. Reinhold, New York (1939).

the transference numbers. The trend toward lower solvation with greater concentration of the cation is to be expected and this trend would cause an opposite trend in transference number with concentration as was found to be the case. Thus the less solvated an ion is the more mobile it should be and, therefore, the data are consistent in these respects.

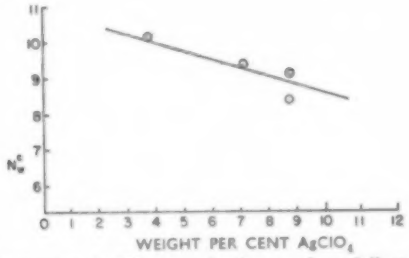

FIG. 2.—Weight per cent $AgClO_4$ vs. solvation number of silver ion, N_w^c, in water.

From the plot of the transference number, t_c, the transference numbers are calculated to be precise to within $\pm 0{\cdot}005$ parts in 0·500 parts or to within 1 per cent. The accuracy is calculated to be about 1 per cent. The precision in 99·7 weight per cent alcohol was only about 8 per cent due to the volatility of the solvent. The solvation data are neither as precise nor as accurate as the transference numbers. In fact both precision and accuracy are estimated to be no better than 10 per cent.

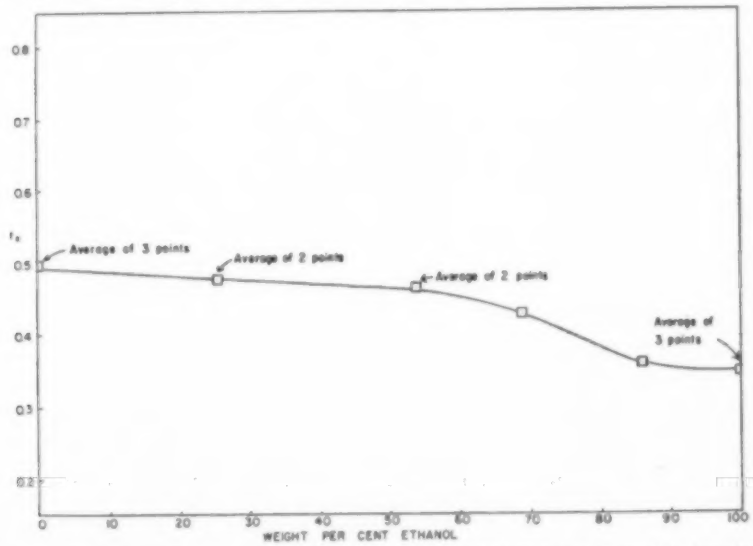

FIG. 3.—Hittorf transference number of the cation, t_c, vs. weight per cent ethanol in the solvent.

Table 2 gives the Hittorf transference number, t_c, of the cation and the change in grammes of solvent per faraday, ΔG_c^F, carried into the cathode compartment in the different solvents. The true transference numbers and apparent solvation numbers of the ions are also given for pure solvents. The transference number of silver ion, at constant concentration of 0·4 molar silver perchlorate, as a function of the weight per cent ethanol is given in Fig. 3. From this figure it is evident that there is first a

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TABLE 2.—HITTORF TRANSFERENCE NUMBER OF THE CATION, t_c, AND THE CHANGE IN GRAMMES OF SOLVENT IN THE CATHODE, ΔG_c^p, PER FARADAY AT 25°C

Wt. ethanol (%)	P_s^m	P_s^c	w^c	w	t_c	α_m	α_c	d_m	d_c	ΔG_c^p	ΔN_c^p	N_c	N_a	$\gamma_\pm$
0·0	7·175	6·645	168·71	0·9866	0·499	18·319	18·260	1·0653	1·0699	83·4	4·64	†9·34		0·497
0·0	7·294	6·580	167·24	1·2536	0·511									
0·0	7·186	*7·730	*166·69	1·0899	0·492									
25·5	7·640	6·976	163·55	1·2116	0·478									
25·5	7·640	6·966	165·60	1·1630	0·474									
54·0	8·059	7·328	152·40	1·1863	0·467	7·311	7·347	0·97493	0·96953	−36·				
54·0	8·059	7·322	153·30	1·0475	0·465	7·311	7·349	0·97493	0·96965	−43·				
69·0	7·772	7·131	145·69	·9243	0·430	6·9145	6·9536	0·89456	0·89005	−116·				
85·8	8·193	7·666	220·57	1·0291	0·360									
99·7	8·954	8·137	137·72	·9946	0·353									
99·7	8·913	8·009	137·75	1·0206	0·368									
99·7	8·740	8·151	207·50	1·0282	0·322	5·2589	5·3003	0·86069	0·85573	−158·	−3·43		‡5·1	0·315
99·7	9·593	8·663	135·21	1·0687	0·323									

* Anode.
† N_a assumed to be zero.
‡ N_a assumed to be zero.

small linear decrease of the transference number of the silver ion with increasing weight per cent ethanol out to about 55 weight per cent ethanol. In this region there is an acceleration of the rate of decrease of the transference number with increasing weight per cent ethanol up to about 85 per cent weight ethanol when the rate of decrease decelerates. From Table 2 it is seen that there is little tendency for the transference number of silver ion in ethanol to change with changing salt concentration. As to rapid change in t_c at about 55 weight per cent ethanol, other chemical phenomena have been found to change radically in the region of 60 weight per cent organic component-in-water solvent.[11,12]

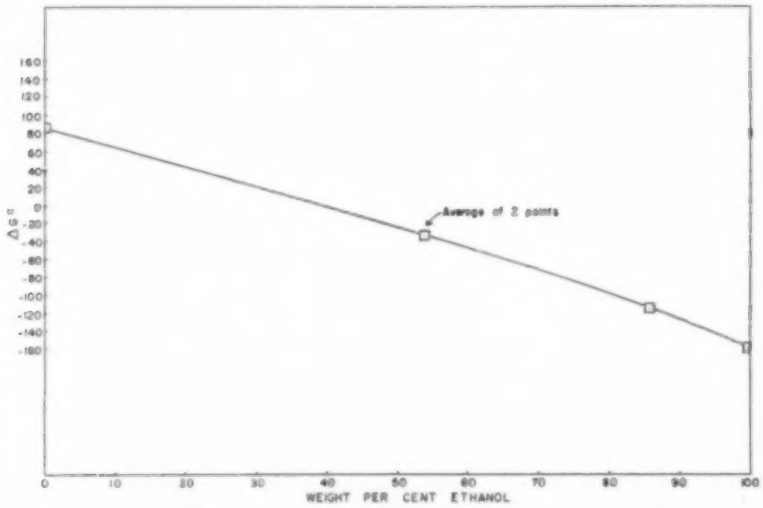

FIG. 4.—Change in grammes of solvent per faraday transported into the cathode portion as a function of the weight per cent ethanol.

While it is known[13] that the inert substance used has some influence on the value of the transference number found in the case of certain ions, yet the two different reference substances used in these experiments did not markedly influence the values of t_c. This is evident since in pure water one of three determinations of t_c involved the use of raffinose and two determinations did not. Yet the agreement of the three determinations is within 1 per cent. (See first three values of t_c in Table 2.) One of the two points in 54 weight per cent ethanol involved the use of raffinose and the other did not and yet the agreement in the two points was within 0·2 per cent. Also one of the three points at 99·7 weight per cent ethanol was made with α-methyl-D-glucoside and two without the inert substance and the agreement of the three data is within 8 per cent, whereas the overall change of the transference number with weight per cent ethanol is about 40 per cent. Thus the general shape of the curve in Fig. 3 is independent of the presence or absence of inert substance.

From Table 2 and Fig. 4 it can be noted that the grammes of solvent carried by the cation into the cathode portion per faraday is a positive quantity in pure water

[11] E. S. AMIS, *J. Phys. Chem.* **60**, 428 (1956).
[12] D. M. MATHEWS, J. D. HEFLEY and E. S. AMIS, *J. Phys. Chem.* **63**, 1236 (1959).
[13a] L. G. LONGSWORTH, *J. Amer. Chem. Soc.* **69**, 1288 (1947); [b] C. H. HALE and T. DEVRIES, *J. Amer. Chem. Soc.* **70**, 2473 (1948); [c] P. Z. FISHER and T. E. KOVAL, *Bull. Sci. Univ. Kiev.* No. 4, 137 (1939).

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and becomes smaller with increasing alcohol concentration. This results in the calculated moles of water per mole of cation being 9·34, if it is assumed that the perchlorate ion is not solvated by water. When the solvent is 54 weight per cent ethanol, the grammes of solvent carried by the cation is a negative quantity, and it is observable that this quantity becomes increasingly negative with increasing alcohol concentration. In 99·7 weight per cent ethanol the grammes of solvent transported is −158. These negative quantities simply mean that at the recorded weight per cents of ethanol in the solvents, the anion carries more solvent into the anode region than the cation carries solvent into the cathode region, and the excess of solvent carried by the anion increases with increasing weight per cent ethanol.

If it is assumed that silver ion is not solvated by ethanol the −158 g corresponds to a solvation number of 5·1 moles of ethanol per mole of perchlorate ion. If the silver ion is solvated with 9·3 moles of alcohol as it calculates to be with water, the perchlorate ion would be solvated with 9·3 moles of ethanol.

For pure solvents, the true transference numbers and the solvation number could be calculated. However, in the mixed solvents these could not be calculated since the molecular weights of the transported solvent to be used in equation (11) and (12) were not known. The molecular weights were not calculable because the composition of the solvent shells about the ions were not known.

These data could be interpreted to mean preferential solvation of the silver ion by water and of the perchlorate ion by ethanol. Selective solvation of ions has been postulated to account for other chemical phenomena.[14,15]

Another possible explanation of the negative values found for the transport of solvent from the cathode region, is that in solvents 54 or greater weight per cent in ethanol the silver ions carry inert reference material into the cathode region. This would give the same effect as perchlorate ions carrying solvent from the cathode region. LONGSWORTH[13a] intimates that the reference substance is not necessarily electrically inert, and that there could, therefore, be association of the ions with the reference substance. However, the magnitude of the effect as recorded by LONGSWORTH would be too small to account for the large effect observed in this research.

It should be mentioned that silver perchlorate in 54 or greater weight per cent ethanol gave a faint yellow colour.

Acknowledgements—The authors are grateful to the United States Atomic Energy Commission for Contract AT-(40-1)-2069 which supported this research financially. The authors also wish to thank Mr. C. V. MCNULLY for carrying out some of the experimental details.

[14] E. S. AMIS, *J. Chem. Phys.* **26**, 880 (1957).
[15] E. S. AMIS, *J. Phys. Chem.* **60**, 428 (1956).

J. Inorg. Nucl. Chem., 1960, Vol. 16, pp. 124 to 130. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES ON METALLIC AZIDES—V*

A STUDY OF CUPRIC AZIDE REACTION

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(*Received* 1 *April* 1960)

Abstract—Spectrophotometric studies have revealed that the yellow colour formed on mixing dilute aqueous solutions of copper (II) chloride and sodium azide is due to a mono-azido-copper complex, with an absorbancy maximum at 367·5 mμ whose formation constant, K has a mean value of (3·724 $\pm$ 0·08) $\times$ $10.^{-3}$ The colour intensity is decreased by the addition of acids and salts furnishing hydrogen, chloride and sulphate ions, but not appreciably by perchlorate or nitrate ions. In the presence of a large excess of azide ions and an appreciable amount of hydrochloric acid, copper (II) can be estimated readily in aqueous solutions in the concentration range of 1–320 p.p.m. spectrophotometrically. The least detectable increment is 1 p.p.m. in the range of 1–10 and 2 p.p.m. in the range of 10–20 p.p.m.

CURTIUS and RISSOM[1] in 1898 were the first to prepare cupric azide from aqueous solution of copper sulphate and sodium azide or by the action of hydrazoic acid on copper. It has also been obtained[2] by the electrolysis of a solution of ammonium azide in liquid ammonia, at -67°C using copper anode.

The yellow-green powder obtained by CIRULIS and STRAUMANIS[3] by the hydrolysis of $Cu(NH_3)_2(N_3)_2$ was assumed to be a basic cupric azide having the formula $Cu(N_3)_2 \cdot 2Cu(OH)_2$. Apart from these compounds cupric azide forms a variety of complexes,[4] e. g., penetration complexes such as the blue crystalline tetrammino-cupric azide $[Cu(NH_3)_4](N_3)_2$, non-electrolytes with the general formula $[(N_3)_2Cu(amine)_2]$ and binuclear complexes with the general formula $[(N_3)_2Cu(amine)Cu(N_3)_2]$.

In 1943 STRAUMANIS and CIRULIS[5] prepared some azido cuprates of the elements of the first and second groups of the periodic system, e.g. lithium hexazido-cuprate, $Li_4[Cu(N_3)_6]$, $3H_2O$; barium tetrazido-cuprate, $Ba[Cu(N_3)_4]$; sodium triazido-cuprate, $Na[Cu(N_3)_3]$ and rubidium pentazido-cuprate, $Rb[(N_3)_2CuN_3Cu(N_3)_2]$. In the first group the number of azide ions per copper atom increased with decreasing cation radius.

Spectrophotometric titrimetry of cupric perchlorate by sodium azide in 80 : 20 vol. 2-ethoxyethanol : water carried out by SAINI and OSTACOLI[6] indicated the formation of CuN_3^+ and suggested the presence of higher complexes such as $[Cu_2(N_3)_5]^-$, $[Cu(N_3)_4]^{2-}$, $[Cu(N_3)_3]^-$, and $[Cu(N_3)_6]^{4-}$ ions. Spectrophotometric measurements in aqueous solutions showed the formation of the complex ion CuN_3^-. The stability constant of this complex had the value of $2{\cdot}3 \times 10^2$ at ionic strength 0·20 and $2{\cdot}8 \times 10^2$ at ionic strength 0·10. The values of pK, extrapolated to zero ionic strength, lie in the range $-2{\cdot}9$ to $-3{\cdot}0$ at 20°C.

* Parts I—IV: H. K. EL-SHAMY and F. G. SHERIF, *Egypt. J. Chem.* 1958 (1959).

[1] T. CURTIUS and J. RISSOM, *J. Prakt. Chem.* (2), **58**, 277 (1898).
[2] A. W. BROWNE and co-workers, *J. Amer. Chem. Soc.* **41**, 1769 (1919).
[3] A. CIRULIS and M. STRAUMANIS, *Z. Anorg. Chem.* **251**, 332 (1943).
[4] M. STRAUMANIS and A. CIRULIS, *Z. Anorg. Chem.* **251**, 335, 341 (1943).
[5] M. STRAUMANIS and A. CIRCULIS, *Z. Anorg. Chem.*, **252**, 9, 121 (1943).
[6] G. SAINI and G. OSTACOLI, *J. Inorg. Nucl. Chem.* **8**, 346 (1958).

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Parallel to the azido-cuprates a series of cupric thiocyanate complexes also exist. Thus cupric thiocyanate complexes were examined spectrophotometrically[7] at 443 mμ using the method of JOB. The data indicated that, in acetone–water mixtures of various SCN^-/Cu^{2+} ratios, two species were important: $[Cu(SCN)_3]^-$ and $[Cu(SCN)_4]^{2-}$. Examination of the entire visible spectrum at different SCN^-/Cu^{2+} ratios indicated that in water solutions of copper (II) thiocyanate the predominating species were Cu^{2+} and $[Cu(SCN)_3]^-$.

Further work on the azide complexes seems desirable. For this purpose spectrophotometric and physico-chemical investigations have been carried out in this laboratory with a view to ascertain the exact nature, stability and structure of any azido-copper (II) complexes that might exist in aqueous or solvent–water mixtures of different compositions and concentrations. The present work is concerned with the study of the nature and absorption properties of the yellow colour formed on mixing aqueous solutions of copper (II) chloride and sodium azide.

EXPERIMENTAL

Reagents and procedure

A stock solution of cupric chloride was prepared by dissolving the AnalaR grade product in redistilled water containing a minimum amount of hydrochloric acid to prevent hydrolysis but insufficient to reduce stability of the resulting yellow copper azide solutions. More dilute solutions were prepared by dilution. In every case the copper content was determined gravimetrically as cuprous thiocyanate. A stock solution of sodium azide was prepared and analysed volumetrically for the azide content by direct titration against standard silver nitrate solution using potassium chromate as indicator. More dilute azide solutions were prepared by dilution and checked for the azide content prior to use.

Other reagents used were prepared from the AnalaR or similar grades.

In carrying out absorbancy measurements, the various copper azide solutions were prepared by mixing the appropriate amounts of stock solutions and diluting to the desired volumes. The colour intensities were measured by means of a Unicam Quartz model S.P. 500. Two glass cells of 1 cm thickness, were used; one for the test solution and the other for the blank. For moderate concentrations of too intense colour, glass plungers of 0·9 cm thickness were dipped in the cells to permit a light path of 0·1 cm. The results are expressed in terms of optical density, D. Measurements were carried out at wavelengths between 330–420 mμ, in which region there was selective absorption for the system investigated. The negligible small absorption of copper chloride at the given concentrations within this wavelength range, permitted the use of redistilled water in the blank cell.

SPECTROPHOTOMETRIC DATA

Absorption spectrum

Equimolecular volumes of cupric chloride and sodium azide solutions were mixed to give a cupric azide solution, 0·01 M with respect to copper and azide ions and 0·000305 M with respect to hydrochloric acid. The absorbancies were measured immediately after mixing. The absorbancy maximum for the yellow colour of cupric azide solution lies at a wavelength of 367·5 mμ.

Nature of colour reaction

It is assumed that cupric azide solutions contain a series of complexes of the general formula: $Cu(N_3)_x^{(2-x)^+}$ where x is an integer from 1 to 4, it is possible to represent the stability constants of such complexes by the expression:

$$K_x = \frac{[Cu(N_3)_x^{(2-x)^+}]}{[Cu(N_3)_{(x-1)}^{(3-x)^+}]\,[N_3^-]}$$

[7] Compt. Rend. 78e Conger. Socs. Savantes Paris et dépts., Sect. Sci, 373-80 (1953).
[8] J. H. YOE and A. L. JONES, *Industr. Engng. Chem. (Analyt.)* **16**, 111 (1944).

If the complex has no real existence, K will be equal to zero. It is clear from this equation that the relative proportions of the different complexes, though dependent on the azide concentration, are quite independent of the Cu^{2+} concentration so long as the latter is not sufficiently great to reduce appreciably the azide concentration by complex formation. This effect was demonstrated by performing two series of experiments. In one series the amount of copper was kept at 0·0002 M, hydrochloric acid at 0·000427 M and that of azide was varied from 0·002 to 0·020 M. In another series, the azide concentration was kept constant at 0·020 M, the hydrochloric acid at 0·000427 M and the cupric ion concentration varied from 0·00008 to 0·0002 M. The optical density (D) of the solutions of both series was measured over the wavelength range of 330–430 mμ. The results are represented graphically in Figs. 1 and 2.

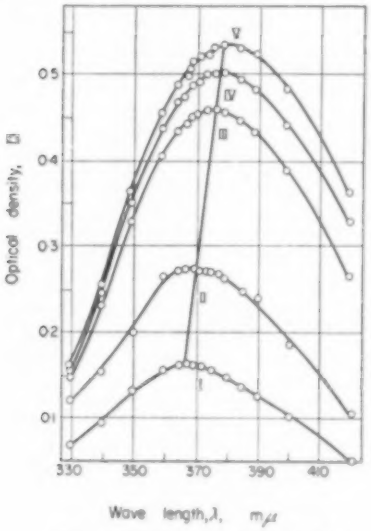

FIG. 1.—Variation of the absorbancy of cupric azide solutions (Cu^{2+} = 0·0002 M; H^+ = 0·000427 M) with increasing concentration of azide ion. (N_3^- (I) 0·002 M; (II) 0·004 M; (III) 0·012 M; (IV) 0·016 M; (V) 0·020 M.)

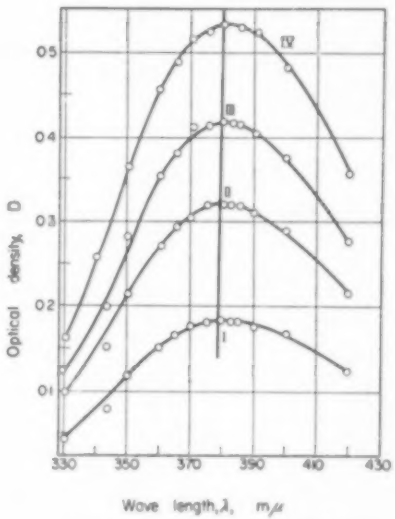

Fig. 2.—Variation of the absorbancy of cupric azide solutions (N_3^- = 0·020 M; H^+ = 0·000427 M) with increasing concentration of cupric ion (Cu^{2+} (I) 0·00008 M; (II) 0·00012 M; (III) 0·00016 M; (IV) 0·0002 M.)

Reference to the curves in Fig. 1 shows a significant shift of the absorbancy maximum towards longer wavelengths with increase in azide concentration, indicating a change in the proportions of the various complexes. By contrast, maxima in Fig. 2 remain constant. Thus the above predictions are confirmed.

Sensitivity of the reaction

A series of experiments were carried out in 100 ml tall-form Nessler tubes using different copper concentrations. It was found that the limit of sensitivity of the test for copper as cupric azide is 1 p.p.m. when viewed by the naked eye. The azide concentration should be in large excess (at least 200 moles azide/mole Cu^{2+}). An acid concentration of about 0·0004 M should also be present. Hydrochloric acid is preferred. Independent observers were able to detect the colour easily and to distinguish it from a reagent blank. The optimum concentration range for comparison in Nessler tubes is 1–20 p.p.m. of copper present as copper (II). The least detectable increment is 1 p.p.m. in the range of 1–10 and 2 p.p.m. in the range of 10–20.

Confirmity to Beer's law

To test confirmity to Beer's law, three series of experiments were carried out.

(1) A cupric azide solution, prepared by mixing equal volumes of equimolecular solutions

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containing Cu^{2+} and N_3^- ions, was successively diluted with redistilled water and the optical densities measured after each dilution.

(2) A cupric azide solution containing a large excess of azide, to ensure the saturation of the colour, was treated similarly. In neither case was Beer's law found to hold. The non-conformance is believed to have been due to the change in acid concentration on dilution or to the effect of a time factor during successive dilutions.

(3) Beer's law was found, however, to hold strictly only when the freshly prepared cupric solutions of varying dilutions were treated with the appropriate amounts of hydrochloric acid and a substantial excess of azide solution and the optical density measured immediately after mixing. Beer's law was found to hold for concentrations of cupric copper between 1–320 p.p.m. A straight line with a zero intercept value was obtained at a wavelength of 370 mμ. Cu^{2+} concentrations above this range were found to cause a slight deviation.

Factors affecting the stability of colour

(a) *Effect of hydrochloric acid.* Varying amounts of hydrochloric acid solution, up to 0·0012 M, were added successively to a series of cupric azide solutions, 0·01 M (containing Cu^{2+} and N_3^- ions in equimolecular ratios). The same procedure was carried out with cupric thiocyanate solutions of the same concentrations and compositions. The colour intensities of cupric thiocyanate solutions were found to increase gradually to a flat maximum, with increasing hydrochloric acid content, and then to decrease slowly. By contrast, the colour intensities of cupric azide solutions were found to increase to a maximum corresponding to 0·0003 M HCl and then to decrease sharply as more acid was added. The acid concentration necessary for development of maximum colour intensity corresponds to 3 per cent of the cupric ion concentration and was found to be the optimum concentration to prevent the formation of hydrolysis products.

(b) *Effect of anions.* Cupric azide solutions containing equimolecular concentrations of Cu^{2+} and N_3^- were next prepared from various copper salts in order to evaluate the effect of the anion upon colour intensity. The colour intensities as measured at a wavelength of 370 mμ, were found to decrease in the order: perchlorate > nitrate > chloride > sulphate. This variation in intensity is attributed to the effect of the different anions. Similiar effects were observed when cupric azide solutions were prepared containing varying amounts of perchloric, nitric, hydrochloric or sulphuric acid.

(c) *Effect of* pH. Cupric azide solutions containing equimolecular concentrations of Cu^{2+} or N_3^- ions were prepared in buffered media at different pH values. The results showed that below pH 3, the cupric azide colour was completely destroyed. The colour intensity, however, was found to increase gradually with rise of pH, in the case of non-complexing acetate buffers, up to pH 8 where precipitation started to take place. In the complexing phosphate-citrate buffers the azide complex was destroyed.

(d) *The effect of time, light and temperature.* In general solutions containing a large excess of azide or copper were found to be stable on standing. Solutions exposed to daylight decomposed to a greater extent than those kept in the dark. Solutions containing hydrochloric acid were found to fade in colour with rise of temperature. Precipitation always took place when unacidified solutions or those favouring the formation of $Cu(N_3)_2$ were heated.

DEGREE OF IONIZATION AND EQUILIBRIUM CONSTANT

The cupric azide complex was investigated at low concentrations of cupric ion in an acid medium. If the $[Cu(N_3)]^+$ species is assumed to be present in solution the equilibrium constant, K, for the dissociation reaction can be given by

$$K = \frac{(a - x)(b - x)}{x} \tag{1}$$

where a and b are known in terms of the molar concentrations, and x in terms of absorption at a given wavelength. At the saturation value of the colour, the absorption value D would be proportional to the concentration a. Any absorption value reading d less than this saturation value would be proportional to x which can be evaluated in terms of the molar concentration using the relationship:

$$x = a\,\frac{d}{D}\ \text{mole/l.} \tag{2}$$

Since a, b and x are known, the value of K can be evaluated.

Standard cupric chloride solutions, 0·0002 M with respect to Cu^{2+} and 0·000006 M with respect to HCl, were prepared containing variable amounts of sodium azide, up to a molar ratio of N_3^-/Cu^{2+} equal to 220. The absorbancy of each solution was measured at a wavelength of 370 mμ. The experimental results are shown graphically in Fig. 3. The colour saturation value was obtained by extrapolation. The continuous increase in intensity with increase in azide ratio shows that the cupric azide complex is highly dissociated. The value for x in equation (2) were calculated and found

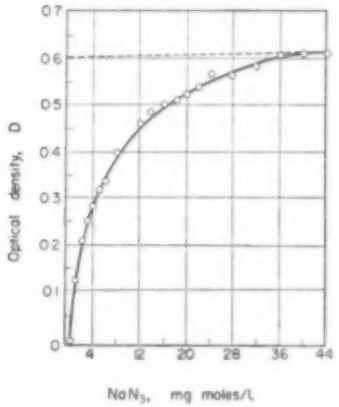

FIG. 3.—Absorbancies of cupric azide solutions (Cu^{2+} = 0·0002 M) as a function of increasing azide ion concentration. (N_3^- = 0·00 to 0·044 M) at 370 mμ.

to remain fairly constant up to a N_3^-/Cu^{2+} molar ratio of fifteen, showing that formation of mono-azido-copper (II) complex over this concentration range is a permissible assumption. However, for molar ratios greater than fifteen, complexes containing more than one co-ordinated azido group may be present, as shown in Fig. 1, where the N_3^-/Cu^{2+} molar ratio reaches 100. The calculated values of the equilibrium constants for other molar ratios, $n = 2$ (e.g. K' for $Cu(N_3)_2$), show no agreement with variation in N_3^-/Cu^{++} ratios. Values for both K and K' are given in Table (1). The mean value of K was found to be $(3{\cdot}724 \pm 0{\cdot}08) \times 10^{-3}$.

TABLE 1.—EQUILIBRIUM CONSTANTS OF CUPRIC AZIDE SOLUTION

$Cu^{2+}:N_3^-$	Mole fraction Cu^{2+}	$K \times 10^3$	$K' \times 10^6$
1:1	0·50	3·673	0·698
1:2	0·33	3·662	1·396
1:3	0·25	3·691	2·115
1:4	0·20	3·682	2·818
1:5	0·167	3·599	3·450
1:6	0·143	3·696	4·254
1:8	0·111	3·741	5·768
1:10	0·09	3·706	7·152
1:12	0·077	3·814	8·845
1:14	0·067	3·913	10·640
1:15	0·0625	3·810	11·100

DISCUSSION OF THE RESULTS

The formation of a coloured azido-copper (II) complex is the result of a number of competitive reactions. If x water molecules are considered to be co-ordinated with every copper (II) ion, then the displacement of aquo groups from this aquated complex

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by N_3^- ion will result in the production of the coloured aquo azido copper (II) complex as shown by the following equilibrium:

$$[Cu(H_2O)_x]^{2+} + N_3^- \rightleftharpoons [Cu(H_2O)_{x-1}(N_3^-)]^+ + H_2O \quad (5)$$

The gradual increase in colour intensity through increase in azide ion concentration suggests competition between the azide ion and water for a place in the co-ordination sphere. Since the aquated Cu(II) complex acts as Bronsted acids according to the reaction:

$$[Cu(H_2O)_4]^{2+} + H_2O \rightleftharpoons [Cu(OH)(H_2O)_3]^+ + \overset{+}{H_3O} \quad (6)$$

an acid such as hydrochloric acid will inhibit this hydrolysis process. In dilute solutions, precipitation of a basic cupric azide of the undefined composition takes place by the addition of azide ions when insufficient hydrogen ion is present to repress hydrolysis. In fairly concentrated solutions, displacement of hydroxo groups from the hydrolysed species in (6) takes place at high concentrations of azide, thus:

$$[Cu(OH)(H_2O)_3]^+ + N_3^- \rightleftharpoons [Cu(N_3)(H_2O)_3]^+ + OH^- \quad (7)$$

When the azide concentration is high, fewer water molecules would be expected to be left within the complex and so less hydrogen ion would be necessary to prevent hydrolysis, consequently a more intense colour is seen. This indicates that the stability of cupric azide solutions is controlled by the hydrogen ion concentration as well as by the concentration of azide ion present.

In solutions of cupric azide containing equimolecular ratios of Cu(II) and azide ions, the most intense colour appears only at an acid concentration of about 3 per cent that of either copper (II) or azide concentrations; at lower acid concentrations, hydrolysis takes place. On the other hand, at higher acid concentrations, (>3% Cu^{2+}) the ionization of hydrazoic acid is repressed, due to the fact that hydrazoic acid is weak acid ($K = 1{\cdot}8 \times 10^{-5}$) and that it is quite volatile (b.p. 37°C).

The effect of hydrochloric acid on cupric azide solutions is much more pronounced than on cupric thiocyanate owing to the fact that hydrazoic acid is a weaker acid than thiocyanic acid. The less intense colour at high acid concentrations is due also to a competition between the azide and chloride ions in the formation of the azido versus the chloro complexes of copper (II). The formation of the chloro complex of copper (II) is favoured by high concentrations of chloride ion as confirmed by the fact that the colour intensity decreases upon the addition of sodium chloride solution to the cupric chloride solution. The following reactions are thus possible:

$$[Cu(H_2O)_4]^{2+} + Cl^- \rightleftharpoons [Cu(Cl)(H_2O)_3]^+ + H_2O$$

$$[Cu(N_3)(H_2O)_3]^+ + Cl^- \rightleftharpoons [Cu(Cl)(H_2O)_3]^+ + N_3^-$$

$$[Cu(OH)(H_2O)_3]^+ + Cl^- \rightleftharpoons [Cu(Cl)(H_2O)_3]^+ + OH^-$$

The influence of the different anions can be explained on a similar basis. Each anion competes with the azide ion on the basis of its inherent tendency to enter the co-ordination sphere. The observed order in effecting the colour intensity of the cupric azide solution can be explained by the fact that perchlorate and nitrate groups are not complexed by copper (II), whereas chloride and, to a larger extent, the sulphate, do form the corresponding complexes. This is in accordance with the work of NELSON

and GANTZ[9] who showed the decreasing order of relative stabilities of Cu(II) complexes to be oxalate, thiocyanate, citrate, acetate, formate, tartrate, bromide, phosphate, sulphate, fluoride, chloride and nitrate.

The destructive effect of citrate and acetate used in buffer solutions can be explained on the same basis.

[9] P. M. NELSON and E. ST. CLAIR GANTZ. *Proc. Indian Acad. Sci.* **57**, 101 (1947).

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SOME METAL COMPLEXES OF CITRATE—II

ANION EXCHANGE STUDIES*

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Abstract—The anion-exchange behaviour of Co(II), Zn(II), uranyl and Th(IV) was studied in citrate solutions with a strong base anion-exchanger. The highest order complex of Co, Zn and Th with citrate is of the 1 : 2 type. An anionic thorium–citrate complex is formulated to be $Th(Cit')(Cit)^{3-}$. Uranyl forms only a 1 : 1 complex with citrate.

Studies by cation-exchange and potentiometric methods[1,2] have shown that Co(II), Zn(II) and uranyl react in a 1 : 1 mole ratio with the citrate ion. Formation constants of the complexes, $MCit^-$, were determined to be 4·7, 4·7 and 8·5 log units for Co, Zn and uranyl, respectively. Because the complex ions formed are negatively charged, it became of interest to study these ions further by anion-exchange.

Thorium as a tetrapositive ion undergoes extensive interaction with water and with many anions. As part of an investigation of the solution chemistry of thorium, we include here the anion-exchange studies of thorium–citrate complexes.

EXPERIMENTAL

Adsorbabilities were measured with the strong base anion-exchange resin Dowex-1 (polystyrene-divinylbenzene quaternary amine resin, 100–200 mesh). Resin in the citrate form was obtained by treating resin in the chloride form with excess sodium citrate, pH ≏ 8, until the effluent gave negligible chloride test with $AgNO_3$. The resin was then washed with water to remove excess sodium citrate. After resin was air-dried overnight, portions of the resin were analysed for moisture by drying in an oven at 110°, and all resin weights refer to the oven-dried material.

For study of Co–citrate complex, some experiments were carried out using resin in the chloride form at ionic strength 0·16 and pH 7·2. For these experiments, the resin was put through several ammonium chloride (0·16 M NH_4Cl) washings and finally equilibrated with 0·16 M NH_4Cl. The resin was then filtered through a Büchner funnel, rapidly washed free of adhering salt solution with water and air-dried. The experiments were conducted in 0·01 M sodium diethyl barbiturate buffer solution, pH 7·2.

High activity ^{60}Co, ^{65}Zn were obtained from Oak Ridge National Laboratory. $^{234}Th(UX_1)$ was obtained from uranyl nitrate hexahydrate by a solvent-extraction method using thenoyltrifluoroacetone (TTA). All other chemicals were C.P. grade. The γ-activity of the radioisotopes was measured by counting liquid samples with a sodium iodide scintillation well-counter. Uranium and sodium were determined by means of a polarograph and flame photometer, respectively.

Procedure

Twenty millilitres of aqueous solutions containing sodium citrate and metal ion were equilibrated with resin in 50 ml ground glass-stoppered flasks for 16 hr at 25·0°. The solutions were filtered through glass wool rapidly, and 4 ml aliquots were removed for radio-chemical assay. The amount

* The work reported here was supported by the U.S. Atomic Energy Commission through Contract No. AT-(30-1)-1922.

[1] J. Schubert, E. L. Lind, W. M. Westfall, R. Pfleger and N. C. Li, *J. Amer. Chem. Soc.* **80**, 4799 (1958).
[2] N. C. Li, A. Lindenbaum and J. M. White, *J. Inorg. Nucl. Chem.* **12**, 122 (1959).

of resin in each flask was chosen so that a wide range of citrate concentration could be used without appreciable loss in counting accuracy. The distribution coefficients D (amount of radioactive metal per gramme of dry resin/amount per ml solution) were calculated from the decrease in metal concentration in the aqueous phase. Slight corrections were applied due to the water content of the resin. This correction was necessary only when large amounts of resin were used, and in no case did it exceed 5 per cent.

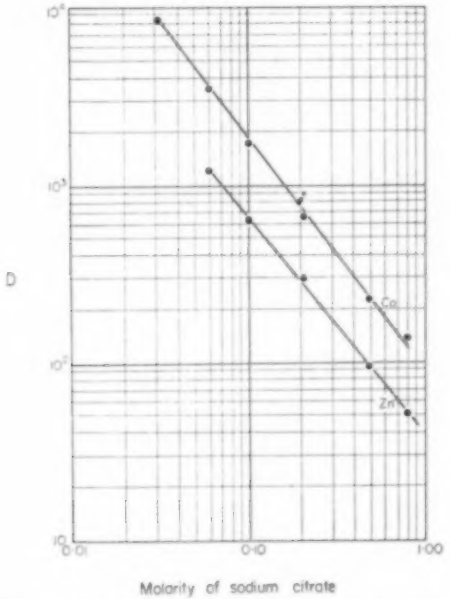

FIG. 1.—Adsorbability of Co(II) and Zn(II) in citrate solutions by Dowex-1 resin citrate.

RESULTS AND DISCUSSION

1. Co(II) *and* Zn(II) *in citrate solutions*

The results are summarized in Fig. 1, a log–log plot of the distribution coefficient D vs. molarity of sodium citrate. Treatment of the data follow that of NELSON and KRAUS[3]. In citrate media we may consider the ion-exchange equilibrium

$$a\mathrm{MCit}_n^{x-} + x(\mathrm{Cit}^{a-})_r = a(\mathrm{MCit}_n^{x-})_r + x\,\mathrm{Cit}^{a-} \tag{1}$$

where MCit^{x-} is the adsorbable complex ion, assumed to be a predominant species, and the subscript r denotes the resin phase. Where no subscript is given, the aqueous phase is implied. The mass action expression for the above equilibrium may be written

$$\frac{K}{G} = \frac{(\mathrm{MCit}_n^{x-})_r(\mathrm{Cit}^{-a})^x}{(\mathrm{MCit}_n^{x-})(\mathrm{Cit}^{-a})_r^x} \tag{2}$$

where K is the exchange constant, G the appropriate activity coefficient ratio.

$$G = \frac{{}^f\mathrm{MCit}_{n,r}^a}{{}^f\mathrm{MCit}_n^a} \cdot \frac{{}^f\mathrm{Cit}^x}{{}^f\mathrm{Cit}_r^x} \tag{3}$$

[3] F. NELSON and K. A. KRAUS, *J. Amer. Chem. Soc.* **77**, 801 (1955).

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Since $(MCit_n)_r$ is small compared with $(Cit)_r$, we may assume that G and $(Cit^{a-})_r$ remain constant, so that equation (2) can be written in the form

$$\frac{K}{G} \times (Cit^{a-})_r^x = \text{constant} = D^a(Cit^{a-})^x \tag{4}$$

since $$D = (MCit_n^{x-})_r/(MCit_n^{x-}) \tag{5}$$

Differentiation of equation (4) gives the equation

$$\frac{d \log D}{d \log (Cit^{a-})} = -x \,|\, a \tag{6}$$

where x is the charge of the adsorbable complex ion and a is the charge on the complexing anion. Fig. 1 shows that the slopes in the log D vs. log (Cit) plots for Co and

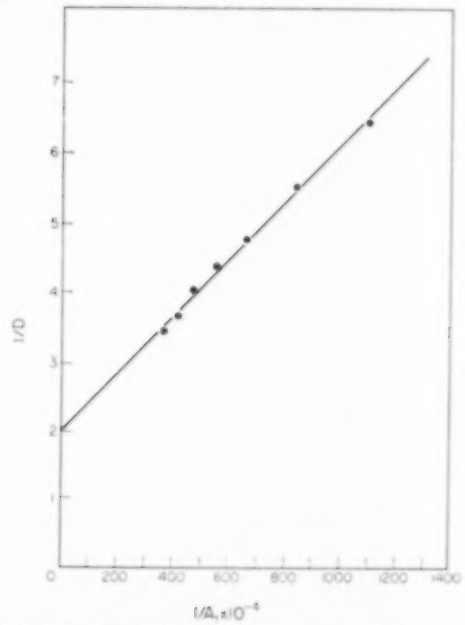

FIG. 2.—Adsorbability of Co(II) in citrate solutions, $\mu = 0{\cdot}16$ pH 7·2 by Dowex-1 resin chloride.

Zn are $-1{\cdot}31$ and $-1{\cdot}25$, respectively, which is close to the theoretical value, $-4/3$, for $-x/a$ of the species $MCit_2^{4-}$. With the resin in the citrate form and in the range of MCit studied (0·03 to 0·8 M), therefore, distribution coefficients decrease with increase in citrate concentration, and the distribution data show that Co and Zn ions form dicitrate complexes in solution.

Studies with Co–citrate complex were also carried out with the resin in the chloride form, $\mu = 0{\cdot}16$, pH 7·2. The results are summarized in Fig. 2 and may be interpreted in the following manner. Consider the ion-exchange equilibrium

$$MCit^- + (Cl^-)_r = (MCit^-)_r + Cl^- \tag{7}$$

$$K = \frac{(MCit^-)_r(Cl^-)}{(MCit^-)(Cl^-)_r} \tag{8}$$

Since (Cl^-) and $(Cl^-)_r$ may be considered constant, we may let $K' = (MCit^-)_r/(MCit)$. With the introduction of the following equations

$$\frac{1}{D} = \frac{(M^{2+}) + (MCit^-)}{(MCit^-)_r} = \frac{M_t \text{ in aq. phase}}{M_t \text{ in resin phase}} \tag{9}$$

$$k_1 = (MCit^-)/(M^{2+})(Cit^{3-}) \tag{10}$$

the following equation results

$$\frac{1}{D} = \frac{1}{K'} + \frac{1}{K'k_1}\frac{1}{Cit} \tag{11}$$

We must also consider the citrate ion itself may be adsorbed and if under the experimental conditions, a constant fraction F of the total citrate A_t remains in the aqueous phase then equation (11) becomes

$$\frac{1}{D} = \frac{1}{K'} + \frac{1}{K'k_1F}\frac{1}{A_t}$$

A plot of $1/D$ vs. $1/A_t$ therefore should yield a straight line and Fig. 2 shows this to be the case. In the concentration range 0·0009 to 0·027 M citrate, therefore, the Co ion forms a monocitrate complex.

TABLE 1.—ANION-EXCHANGE RESULTS FOR THORIUM CITRATE

Na_3Cit (M)	Weight of resin (g)	D
0·2950	0·886	180·5
0·3870	1·012	135·4
0·4823	1·139	104·1
0·5736	1·266	81·2
0·6692	1·583	75·0
0·7582	1·899	64·5

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2. *Thorium–citrate complex*

Table 1 summarizes the data obtained for Th–citrate complex, with the resin in citrate form.

A plot of log D vs. log (Cit) yields a straight line, with slope of -1. From equation (6), $x/a = 1$ and since $a = 3$, x must be 3 also. BOBTELSKY and GRAUS[4] postulate the presence of an anion thorium–citrate complex as $((ThOH)_2Cit_3)^{3-}$, which would fit our value of x. However from certain pH titration data, discussed below, we prefer to formulate the anionic complex as $Th(Cit'\ Cit)^{3-}$, where Cit′ is citrate ion with a charge of -4, i.e. one in which the hydrogen of the hydroxyl group has been displaced.

WARNER and WEBER[5] have shown that citric acid acts as a tetra-basic acid, H_4A, toward Cu(II) and Fe(III), while LI *et al.*[2] state that in the pH region below 9, citric acid acts as H_3A towards Mn, Cd, Zn, Ni and uranyl. The behaviour toward Cu and Zn has been confirmed in our present studies (See Fig. 3 where inflexions occur at

[4] M. BOBTELSKY and B. GRAUS, *J. Amer. Chem. Soc.* **76**, 1536 (1954).
[5] R. C. WARNER and I. WEBER, *J. Amer. Chem. Soc.* **75**, 5086 (1953).

$a = 3$ and 4 for Zn and Cu, respectively). Fig. 4 curve 2 suggests that the dicitrate complex of Cu(II) (inflexion at $a = 7$) may be formulated as $Cu(Cit' Cit)^{3-}$. Since Fig. 4 curve 3 indicates that thorium exhibits the same behavior as Cu(II) (inflexion also at $a = 7$), it becomes reasonable to postulate an analogous formula for the dicitrate complex of Th: $Th(Cit' Cit)^{3-}$. GURD *et al.*[6] have formulated a similar structure for the diglycylglycinate complex of Cu(II) as $Cu(GG' GG)^{-}$, where GG′ is glycylglycinate ion with a charge of −2, one in which the hydrogen from the peptide linkage has been

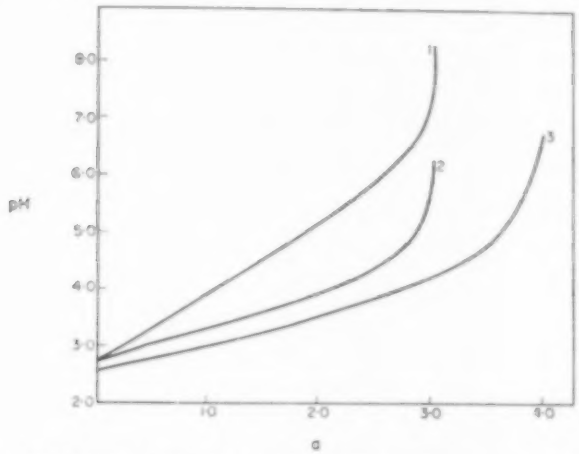

FIG. 3.—Potentiometric titration of: curve 1, 0·010 M citric acid; curve 2, 0·010 M citric acid, 0·010 M $Zn(NO_3)_2$; curve 3, 0·010 M citric acid, 0·010 M $Cu(NO_3)_2$.

displaced. The thorium–citrate complex was also studied by an indirect polarographic method, where the polarographic half-wave potentials of solutions containing 5×10^{-4} M $Cd(NO_3)_2$, 0·05 M sodium citrate and varying concentrations of thorium nitrate were determined. Since thorium itself is not determinable polarographically,[7] the half wave potentials of the solutions are due to the reduction of the cadmium ion and are reversible ($E_{\frac{3}{4}} - E_{\frac{1}{4}} = 0{\cdot}028$–$0{\cdot}031$). As the concentration of thorium increases, the amount of free citrate is decreased because of formation of thorium–citrate complex, and the half wave potential of the solution becomes less negative. Our experimental data show that with an increase in thorium concentration from 0·009 to 0·0275 M, $E_{\frac{1}{2}}$ changes from −0·646 V (S.C.E.) to −0·598 V (S.C.E.) and pH decreases from 6·00 to 3·19. With further increase in thorium concentration (0·05 M sodium nitrate in the presence of 5×10^{-4} $Cd(NO_3)_2$), precipitation occurs.

3. *Uranyl citrate*

Numerous experiments were conducted with the resin in the citrate form under the same conditions as for Co and Zn. However, all the uranyl is taken up by the resin, so that no reasonable distribution coefficients can be obtained. Even in the absence of citrate in the aqueous phase, all the uranyl is in the resin. This extraordinary strong affinity of uranyl to the resin citrate demonstrates that the uranyl–citrate complex must be very stable and is therefore in agreement with the findings of LI *et al.*[2] The

[6] W. L. KOLTUN, M. FRIED and F. R. N. GURD, *J. Amer. Chem. Soc.* **82**, 233 (1960).
[7] I. M. KOLTHOFF and J. J. LINGANE, *Polarography* Vol. 2, p. 446. Interscience, New York (1952).

stability therefore should permit a very effective separation of uranium from other metals by the use of anion-exchangers. The adsorption of uranyl by the resin citrate, when the aqueous solution contains only uranyl chloride, NaCl and no citrate, is in agreement with the statement of Katz and Seaborg[8] that an uncomplexed metal ion in solution may be taken up by an anion-exchanger if the metal ion has a tendency to form anionic complex on the resin itself. The reaction may be formulated as

$$(Cit^{3-})_r + UO_2^{2+} = (UO_2Cit^-)_r$$

Another example of complex ion formation directly at the exchange sites of an ion-exchange resin is the adsorption of uranyl ion from solution by an anion-exchange resin in sulphate form.[9]

$$(SO_4^{2-})_r + UO_2^{2+} = (UO_2(SO_4)_2^{2-})_r$$

The uranyl–sulphate complex like the SO_4^{2-}, is doubly negatively charged and therefore remains sorbed by the anion-exchange resin.

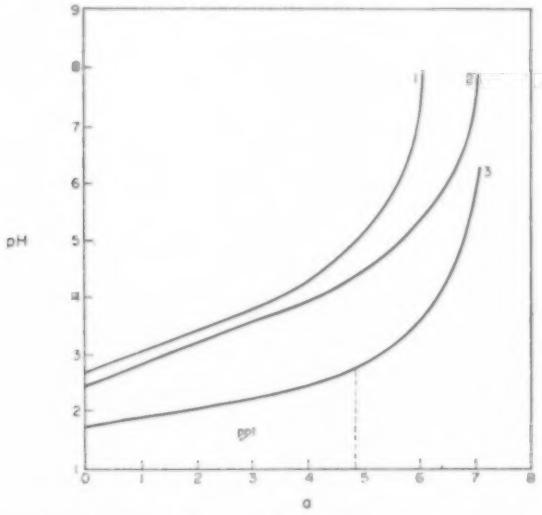

Fig. 4.—Titration of: curve 1, 0·010 M citric acid, 0·0050 M $Zn(NO_3)_2$; curve 2, 0·010 M citric acid, 0·0050 M $Cu(NO_3)_2$; curve 3, 0·010 M citric acid, 0·0050 M $Th(NO_3)_4$, 0·1 M $NaClO_4$.

Li *et al.*[2] have shown that the uranyl–citrate complex is of the 1:1 type and that no 1:2 complex with citrate is formed. In order to further substantiate this point, we have carried out the following experiment: The uranyl–citrate complex was obtained by eluting a cation-exchange resin column (resin in uranyl form) with a small amount of 0·5 M sodium citrate, pH $\simeq$ 8 (0·492 cm^2 $\times$ 28 cm column, flow rate approximately 1 ml/min). The effluent was evaporated to dryness; the yellow solid obtained was dried at 110° for 24 hr, and analysed (Found Na, 5·13; C, 14·30. Calc. for $NaUO_2$ Cit: Na,4·74; C, 14·84%). The analytical data therefore strongly support the finding that uranyl forms a 1:1 complex with citrate.

[8] J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements* p. 116. John Wiley, New York (1957).
[9] T. V. Arden and G. A. Wood, *J. Chem. Soc.* 1596 (1956); W. E. Miller, *Science* **129**, 465 (1959).

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When Dowex-1 resin is in the chloride form and the aqueous phase contains 10^{-3} M uranyl chloride and 0·16 M NaCl, the entire uranium remains in the aqueous phase, demonstrating that the uranyl ion has only slight tendency to enter into complex formation with chloride ion.

Acknowledgements—The authors are indebted to J. RIVERA, R. PFLEGER and M. BECHTOLD for their technical assistance.

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NEPTUNIUM COMPLEX ION SPECIES EXTRACTED FROM NITRIC ACID–PERCHLORIC ACID MIXTURES BY TRIBUTYL PHOSPHATE*

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(*Received* 22 *December* 1959; *in revised form* 2 *February* 1960)

Abstract—Neptunium(IV) and neptunium(VI) were extracted into TBP-xylene from nitric acid–perchloric acid mixtures and the absorption spectra of the neptunium were measured in both phases. The spectra of the neptunium in the TBP solutions were found to vary with the aqueous phase composition. It was concluded that more than one complex ion species extracts in each case and that three neptunium(VI) species are indicated.

RECENTLY the stability of nitrate complexes of thorium[1] and zirconium[2] and the chloride complexes of zirconium[2,3] have been measured by a tributyl phosphate (TBP) extraction procedure. This method[1] depends on the extraction of the tetra-co-ordinated species from an acidic–aqueous phase into a nonmiscible TBP phase. Its application demands that no other species extracts. In practice, extractions have been from solutions in which ionic strength was held constant with perchloric acid.

Spectrophotometric measurements have been made which show that more than one neptunium(IV) and neptunium(VI) complex ion species extracts into TBP from nitric acid–perchloric acid mixtures. This observation raises considerable doubt about the applicability of TBP as an extraction agent for the determination of complex ion stabilities.

EXPERIMENTAL

Neptunium was obtained in nitric acid solution which was converted to perchloric acid solution by successive precipitations of neptunium(V) hydroxide. Neptunium(IV) was prepared by catalytic hydrogen reduction and neptunium(VI) by electrolysis.[4a] A several-fold excess of semicarbazide was added to the neptunium(IV) to act as a holding reductant. Four molar HNO_3 and $HClO_4$ solutions were prepared from Baker and Adamson reagent grade acids. One molar TBP was prepared from redistilled tributyl phosphate and Baker and Adamson reagent grade xylene. Before each neptunium solution was extracted, a portion of TBP was brought to equilibrium with the acid by three successive contactings with equal volumes of acid.

Acid mixtures were prepared at the desired nitrate concentrations, at total acid equal to 4·0 molar and neptunium was added to each mixture. The absorption spectrum was measured from 400 to 1300 mμ with a Cary Model 14 recording spectrophotometer. Each solution was then contacted for 5 min with an equal volume of 1·0 M TBP and the spectrum of each phase was measured. The concentration of the organic phase was determined by radiometric assay. The neptunium concentrations of all aqueous phases, except 4·0 M $HClO_4$, were about 0·008 molar before contacting.

* Work performed under Contract No. AT(45-1)-1350 for the U.S. Atomic Energy Commission.

[1] V. V. FOMIN and E. P. MAIOROVA, *Zh. Neorg. Khim.* **1**, 1703 (1956); AERE-LIB-TR-802 (1958).
[2] A. S. SOLOVKIN, *Zh. Neorg. Khim.* **2**, 611 (1957); AERE-LIB-TR-791 (1958).
[3] A. E. LEVITT and H. FREUND, *J. Amer. Chem. Soc.* **78**, 1545 (1956).
[4a] D. COHEN and J. C. HINDMAN, *J. Amer. Chem. Soc.* **74**, 4679, 4682 (1952); [b] W. C. WAGGENER, *J. Phys. Chem.* **62**, 382 (1958).

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RESULTS AND CONCLUSIONS

The spectra of neptunium(IV) in nitric–perchloric acid mixtures at constant total acid concentration equal to 4·0 M are shown in Fig. 1. These spectra change with solution composition because of nitrate complex formation.

The spectra of neptunium(IV) in 1·0 M TBP are shown in Fig. 2. The neptunium in each solution represented in this figure was extracted from an aqueous solution shown in Fig. 1. The neptunium spectra in the TBP solutions are clearly a function of the composition of the aqueous phase from which the neptunium was extracted. It has been

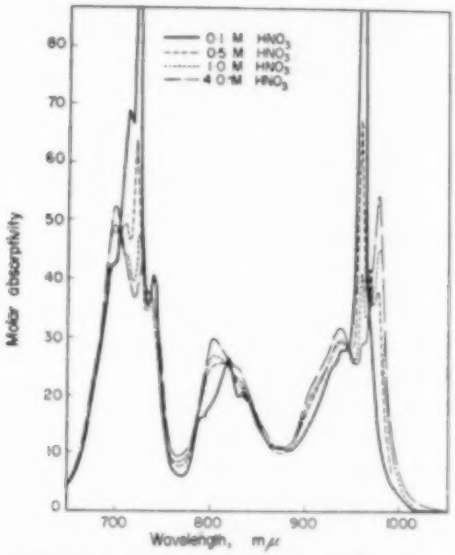

FIG. 1.—Absorption spectra of neptunium(IV) in 4·0 M nitric acid–perchloric acid solutions.

shown that the absorption spectra of ions in solution are very nearly independent of the solvent environment in cases where the particular inner sphere complexes present are not altered.[5] The complex ion species extracted into the TBP must, therefore, change with aqueous solution composition.

No part of these spectra appears to be due to higher oxidation states of neptunium. Neptunium(VI) has no significant absorption peaks in the wavelength region considered. The extractability of neptunium(V) is low and the spectra of the aqueous phases after extraction did not show appreciable amounts of this oxidation state. Since spectral measurements were made immediately following extraction, no neptunium(V) should have appeared in the organic phase. The absence of neptunium(V) absorptions in the TBP spectra is also shown by the following observation. A TBP solution of neptunium(IV) developed new peaks at 980 and 1003 mμ after several days time, but its former spectrum returned when it was back extracted with the original acid solution. The 980 mμ peak of neptunium(V) then appeared in the aqueous solution.

It was expected that $Np(NO_3)_4 \cdot 2TBP$ would be the chief extracted species at all nitrate–perchlorate compositions containing sufficient nitrate to form the complex.

[5] J. BJERRUM, A. W. ADAMSON and O. BOSTRUP, *Acta Chem. Scand.* **10**, 329 (1956).

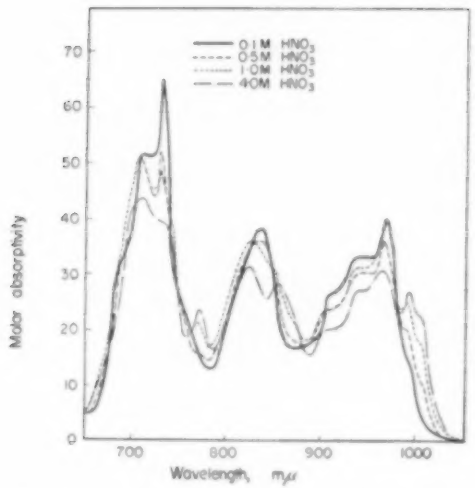

FIG. 2.—Absorption spectra of solutions of neptunium(IV) in 1·0 M TBP extracted from the aqueous solutions in Fig. 1.

Apparently, this is not true. Since only uncharged species are extracted by the unionized TBP, one must conclude that at least one perchlorate-containing complex of neptunium(IV) is extracted.

SOLOVKIN[2] has described a TBP extraction technique for determining stability constants and has measured the stability of four zirconium nitrate complexes. FOMIN and MAIOROVA[1] have employed the same method for determination of the stability of thorium nitrate complexes. In these studies 4·0 M perchloric–nitric acid mixtures were used. It was assumed in the treatment of the data that the tetranitrato complex is the only species extracted. The fact that other species extract in the case of neptunium(IV) raises some question about the validity of this assumption in the cases of zirconium and thorium.

Similar measurements have been made with neptunium(VI). The results are

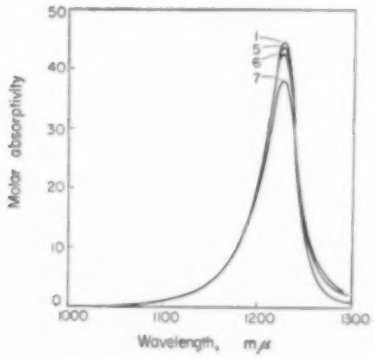

FIG. 3.—Absorption spectra of neptunium(VI) in nitric acid–perchloric acid solutions.
1. 0·00 M HNO_3 + 4·0 M $HClO_4$
5. 0·5 M HNO_3 + 3·5 M $HClO_4$
6. 1·0 M HNO_3 + 3·0 M $HClO_4$
7. 4·0 M HNO_3 + 0·0 M $HClO_4$

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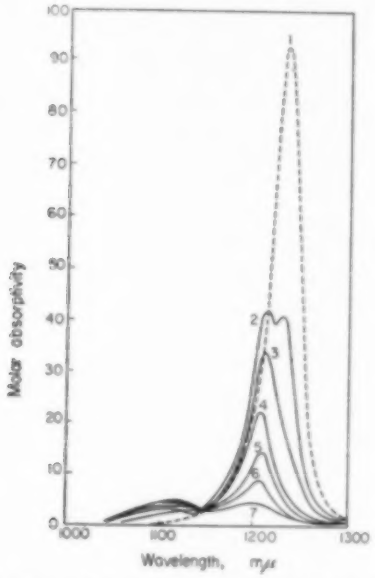

FIG 4.—Absorption spectra of neptunium(VI) in 1·0 M TBP extracted from nitric acid–perchloric acid solutions.
1. 0·00 M HNO_3 + 4·0 M $HClO_4$
2. 0·05 M HNO_3 + 3·95 M $HClO_4$
3. 0·10 M HNO_3 + 3·9 M $HClO_4$
4. 0·3 M HNO_3 + 3·7 M $HClO_4$
5. 0·5 M HNO_3 + 3·5 M $HClO_4$
6. 1·0 M HNO_3 + 3·0 M $HClO_4$
7. 4·0 M HNO_3 + 0·0 M $HClO_4$

shown in Figs. 3 and 4. The spectra at wavelengths shorter than those shown gave no evidence of other oxidation states. Neptunium(VI) is considerably more extractable from $HClO_4$ than neptunium(IV); so, in this case, spectra were obtained over the entire range of acid mixtures from 4·0 M HNO_3 to 4·0 M $HClO_4$.

The spectra of neptunium(VI) in TBP solutions, Fig. 4, indicate that three separate species extract from the acid solutions studied. Neptunium(VI) has been shown to extract from nitric acid as $NpO_2(NO_3)_2 \cdot 2TBP$.[6] A corresponding diperchlorato complex might be expected to be the species extracted from pure perchloric acid. Only one nitratoperchlorato complex is possible. This species seems a more reasonable postulate for the source of the intermediate spectrum that either a charged or hydrolysed TBP complex.

Further work is in progress on the spectra of other actinide oxidation states in TBP solutions.

[6] J. K. DAWSON, R. ELLIOTT and H. A. C. MCKAY, AERE/C/R-1117 (1953).

J. Inorg. Nucl. Chem., 1960, Vol. 16, pp. 142 to 146. Pergamon Press Ltd. Printed in Northern Ireland

PRESSURE-COMPOSITION DATA FOR THE LIQUID HCl–HBr SYSTEM AT DRY-ICE TEMPERATURES*

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(*Received* 14 *January* 1960; *in revised form* 16 *February* 1960)

Abstract—A simple, pressurized thermostat containing solid CO_2 has been used to achieve temperatures accurate to <0·01° in the range −78·4– −79·0°. The vapour-pressure of high purity HBr in this temperature range is given by log $P_{mm} = -9{\cdot}5915 \times 10^3/T + 7{\cdot}5316$. Similar equations are reported for the vapour-pressures of eight mixtures of HCl and HBr and dew point pressures for four. The system shows moderate positive deviation from ideality.

A CONVENIENT means for the analysis of HCl–HBr mixtures is the determination of the vapour-pressure of the condensed liquid.[1] For this purpose a thermostat utilizing solid carbon dioxide (Dry-Ice) is eminently satisfactory. Pure HCl and HBr have vapour-pressures of 1084 and 402 mm at −78·514°, the CO_2 sublimation temperature, and the temperature of the thermostat corresponding to any CO_2 pressure can be accurately determined from the data of MEYERS and VAN DUSEN[2] since dT/dP is −0·016° per mm in this region. In order to make the data useful over a range of barometric pressures, the vapour-pressures have been measured over a minimum temperature range of −78·4 — 79·0°, corresponding to pressures of 767–730 mm. Dew point pressures have also been measured for four mixtures.

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EXPERIMENTAL

Materials

Anhydrous hydrogen bromide was prepared by the reaction of bromine with 1,2,3,4-tetrahydronaphthalene (tetralin).[3] The tetralin (Eastman Kodak, practical) was first dried and distilled in an Oldershaw column, and the all-glass reaction vessel and purification train was evacuated prior to reaction. The evolved HBr passed through a tetralin bubbler to remove Br_2, a −63° trap to condense tetralin, and was collected at −80°. The gas was then pulled through a large, serrated tower containing P_4O_{10} and condensed onto P_4O_{10} with liquid N_2. After thorough evacuation (<10^{-4} mm Hg in all experiments) the HBr was warmed to −80° and the vapour above the liquid slowly removed to a storage flask, discarding the first and last 15–20 per cent. This procedure was designed to remove all water, tetralin and bromine from the product. The fraction saved was then checked for homogeneity by measurement of the vapour-pressure of the most and least volatile fractions obtained at −80°. Initially, a 20–30 mm variation in the pressure was observed and this could be reduced to less than 2 mm only by extensive fractionation at −80 and −126°. The impurity was considered to be HCl, since a chlorine content of 0·3 per cent was allowed in the reagent-grade bromine used and a like amount of chloride could be found in an aqueous solution of the initial product. Therefore, a high-purity Br_2 (A. D. MacKay, <0·02 per cent Cl) was used in the preparation and this was also first

* Contribution No. 834. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

[1] J. D. CORBETT and N. W. GREGORY, *J. Amer. Chem. Soc.* **75**, 5238 (1953).
[2] C. H. MEYERS and M. S. VAN DUSEN, *Bur. Stand. J. Res.* **10**, 381 (1933).
[3] H. S. BOOTH (Editor), *Inorganic Syntheses* Vol. 1, p. 151. McGraw-Hill, New York (1939).

equilibrated with powdered KBr. Variation in the vapour-pressure of the HBr was thereby reduced to 0·5–1 mm, depending on the extent of fractionation.

Hydrogen chloride was prepared by the convention dehydration of conc. aqu. HCl with conc. H_2SO_4 in an evacuated apparatus. The gas was passed through two H_2SO_4 bubblers, two $-80°$ traps, the drying column, and condensed on P_4O_{10} with liquid N_2. The last 15 per cent remaining after vaporization at $-80°$ was discarded; no inhomogeneity could be detected by vapour-pressure measurements. The amount of condensable impurities in commercial hydrogen chloride and hydrogen bromide is relatively large.

Vapour-pressure measurements

The apparatus used is shown in Fig. 1. Manometers 1, 2 and 4 were constructed from selected 8·0 mm i.d. tubing; pressures were read to 0·1 mm on metre sticks previously calibrated with a

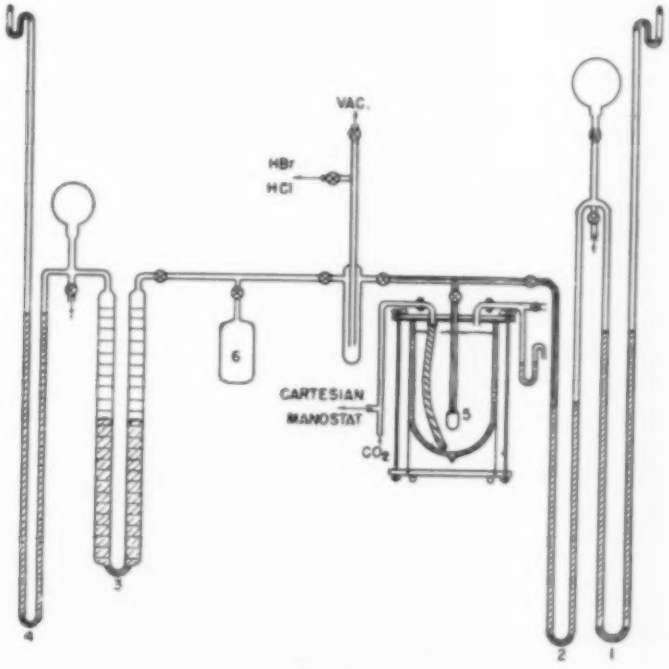

FIG. 1.

precision cathetometer. The vapour-pressure finger (5) was connected to manometer 2 with 2 mm capillary tubing; this and the use of 2 as a differential manometer kept the fraction of any sample in the gas phase below 1 per cent.

The thermostat, a modification of that of BROWN and BRADY[4] consisted of a quart Dewar flask filled with powdered CO_2 and sealed with a split lid covered with soft rubber. The latter was clamped onto the flask by wing nuts on $\frac{1}{4}$ in. steel rods extending to the wooden base; Apiezon "Q" was used to seal any small leaks around the lid. In order to achieve a known temperature all air must be displaced from the flask; for this purpose a rapid stream of gaseous CO_2 (Matheson, "bone-dry"), conducted to the bottom of the flask was found to be superior to the immersed heater usually employed in thermocouple calibrations. Impurities in commercial Dry-Ice have been reported to affect the temperature by $<0·01°$.[2] Alternation between cylinder CO_2 and that generated with a heater indicated that gaseous impurities in the former were negligible, affecting the vapour-pressure of HBr by $<0·3$ mm.

[4] H. C. BROWN and J. D. BRADY, *J. Amer. Chem. Soc.* **74**, 3581 (1952).

After this flushing was complete, a much smaller CO_2 flow was maintained through the flask. For measurements at pressures above atmospheric a Cartesian Manostat (Emil Griener and Co., No. 7A) was used on the inlet stream and the pressure increase noted on the small manometer. Pressure regulation to less than $\pm 0{\cdot}5$ mm up to $+40$ mm could be obtained. Response of the observed vapour-pressure to changes in CO_2 pressure was very rapid. However, the *initial* vapour-pressure observed for a HCl–HBr mixture was always high and decreased to the equilibrium value in about 20 min. The first liquid produced when the solid mixture melted would be lower in both density and HBr content, and this HCl-rich layer apparently persisted on the liquid surface for some time. At constant temperature and composition the same pressure was obtained when the equilibrium was approached from either higher or lower pressures; this was accomplished by momentarily changing either the temperature of the thermostat or the volume available to the gas. Final pressures were constant to $\pm 0{\cdot}1$ mm for greater than 10 min and the thermostat could be used for one and one-half hours before repacking became necessary.

Dew point pressures

A similar though larger thermostat was used about volume 6 (Fig. 1) for these measurements. Manometer 3 was constructed from 100 ml burette tubes, 17 mm o.d., so that appreciable volume changes could be produced. Dew point pressures, corresponding to the formation of the first liquid phase, were evidenced by a sharp decrease in $\Delta P/\Delta V$ to essentially zero as the volume was decreased in 0·2 ml increments. The total gas volume was about 660 ml, 85 per cent of which was cooled by the thermostat. All mixtures were prepared by conventional techniques using ideal P–V relationships.

The barometric pressure was read on a Welch Marine Barometer that had been calibrated by comparison to a high precision barometric calibration standard (Wallas and Tiernan, Model F8187). In addition to the standard barometric scale correction, *all* pressures were corrected to mm of Hg at 0° and to standard gravity, using a locally determined value of g.

RESULTS AND DISCUSSION

The vapour-pressure data obtained for hydrogen bromide in the range $-77{\cdot}7$–$-79{\cdot}0°$ are described by the equation

$$\log P_{mm} = -9{\cdot}5915 \times 10^2/T + 7{\cdot}5316$$

with an average deviation of 0·18 mm for twenty-seven pressures. With $\Delta C_p = -7{\cdot}37$ cal deg^{-1} [5] the data extrapolate to a boiling point of $-66{\cdot}82°$, $0{\cdot}09°$ lower than accepted.[5] The heat of vaporization, 4390 cal mole^{-1}, compares to 4330 cal mole^{-1} previously reported.[6] A significant HCl impurity may have been present in the previous study as the vapour-pressures reported[6] are 2·4 mm higher than those found here with HBr of apparent high purity.

Vapour-pressures obtained for HCl were less than 0·4 mm lower than those calculated from the data of HENNING and STOCK[7] ($\log P_{mm} = -8{\cdot}6381 \times 10^2/T + 7{\cdot}47311$ in this range), the difference being essentially equal to the gravity correction applied.

The data for the HCl–HBr mixtures, 8 to 13 for each composition, are summarized in Table 1. The choice of an equation of the type $\log P = -A/T + B$ was a matter of convenience, and, because of the limited temperature range, the slope A is not accurately related to an apparent heat of vaporization. However, the number of significant figures quoted for A and B are necessary to reproduce the measured pressures. Although $\log P$ vs. $1/T$ plots for mixtures rich in HBr showed some evidence of curvature, this appeared to be within experimental error of the linear relationship

[5] *Selected Values of Chemical Thermodynamic Properties*. National Bureau of Standards, Circ. 500, Series II, Table 10. U.S. Government Printing Office, Washington, D.C. (1952).
[6] J. R. BATES, J. O. HALFORD and L. C. ANDERSON, *J. Phys. Chem.* **3**, 531 (1935).
[7] F. HENNING and A. STOCK, *Z. Physik* **4**, 226 (1921).

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TABLE 1.—VAPOUR-PRESSURES OF HCl–HBr MIXTURES AS LOG $P_{mm} = -A/T + B$, −78·4– −79·0°

Mole % HCl	$A \times 10^{-3}$	B	Average deviation (mm)
$10{\cdot}1_0$	9·7826	7·7169	0·44
$24{\cdot}7_1$	9·8836	7·8593	0·37
$40{\cdot}3_9$	9·6099	7·7911	0·65
$49{\cdot}7_6$	9·6000	7·8239	0·78
$60{\cdot}7_4$	9·6774	7·9030	0·98
$70{\cdot}3_2$	9·4231	7·8022	0·63
$80{\cdot}0_2$	9·1667	$7{\cdot}6973_6$	0·38
$90{\cdot}2_2$	8·9394	$7{\cdot}6054_7$	0·23

employed; a small change in sample composition with increasing vapour-pressure might be responsible.

Dew point pressures were investigated less extensively; the data for the four mixtures studied are listed in Table 2. The equation $1/T = 74{\cdot}1416\ (9{\cdot}81018 - \log P_{CO_2})$, derived from Ref. (2), can be used to relate the pressure data in Tables 1 and 2 directly to P_{CO_2}.

TABLE 2.—DEW POINT PRESSURES OF HCl–HBr MIXTURES AS LOG $P_{mm} = -C/T + D$, −78·5 to −78·9°

Mole % HCl	$C \times 10^{-3}$	D	Average deviation (mm)
$24{\cdot}6_7$	7·4340	6·5064	0·3
$37{\cdot}8_3$	$10{\cdot}707_6$	8·2420	0·5
$54{\cdot}0_8$	$13{\cdot}431_0$	9·7221	0·3
$75{\cdot}0_7$	$10{\cdot}169_9$	8·1438	1·0

The pressure-composition diagram (Fig. 2) illustrates the moderate positive deviation from ideality found in this system. These results bear no relationship to the results of KLEMANC and KOHL[8], who, on the basis of vapour-pressure deviations between about 46 and 54 mole per cent, claimed that a solid 1:1 compound was formed between −70 and −100°. The presence of gross impurities seems to be the only explanation for their observations. However, a positive deviation in vapour-pressures only slightly larger than that reported here was found at −86·4° by ALTMAN[9], although his description of the vapor pressures in terms of symmetrical activity coefficients in a Margules-type equation[10] is not in exact agreement with the present results.*

If gaseous HCl and HBr are assumed to mix ideally, activity coefficients for the

* For agreement to ±2 mm, ALTMAN found $\beta = 0{\cdot}25$; here, $\beta_{HCl} \cong 0{\cdot}18$, $\beta_{HBr} \cong 0{\cdot}30$. In both cases the individual gas imperfections were corrected by means of Berthelot's equation. ALTMAN also had to correct observed pressures for temperature variations of ±0·1° in the trichlorethylene slush bath, and the source of the hydrogen halides used was not stated.

[8] A. KLEMANC and O. KOHL, *Z. Anorg. Chem.* **168**, 163 (1927).
[9] D. ALTMAN, U.S.A.E.C. Document AECD-2681, Technical Information Service, Oak Ridge, Tenn. (1945).
[10] J. H. HILDEBRAND and R. L. SCOTT, *The Solubility of Nonelectrolytes* (3rd Ed.), pp. 35–38. Reinhold, New York (1950).

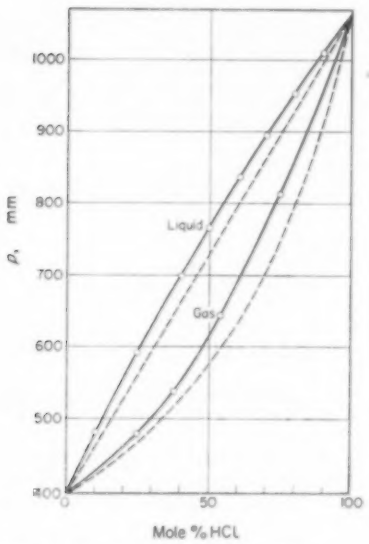

FIG. 2.—The HCl–HBr system at −78·87°. The broken curves represent ideal behaviour.

liquid components can be calculated directly from the liquid and gas compositions. However, the resulting coefficients* are not consistent with the Gibbs–Duhem equation[10] for mixtures containing less than about 50% HCl. The self-consistent coefficients above this composition as well as the form of the equation describing the vapour-pressures† nevertheless indicate that HBr shows the greater positive deviation in this system. The lack of complete consistency between the calculated activity coefficients may be due to non-ideal gas behaviour. Although significant deviations are known for gaseous HCl and HBr (0·971 and 0·980 for PV/RT at −78·5° and the respective vapour-pressures[11]), additional nonideal mixing would be necessary to account for the results. On the other hand, though the vapour-pressure data are considered quite reliable, insufficient data for the somewhat unusual form of the gas composition curve (Fig. 2) may be responsible.

Acknowledgement—The guidance and interest of Professor N. W. GREGORY in a preliminary investigation of this problem are gratefully recognized.

* E.g. $\gamma_{HCl} = 1{\cdot}12, 1{\cdot}005, 1{\cdot}00$; $\gamma_{HBr} = 1{\cdot}02, 1{\cdot}19, 1{\cdot}26$ (pure liquids) at 10, 50 and 90% HCl, respectively.

† See footnote on p. 145.

[11] C. F. CURTISS and J. O. HIRSCHFELDER, *J. Chem. Phys.* **10**, 491 (1942).

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J. Inorg. Nucl. Chem., 1960, Vol. 16, pp. 147 to 161. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

A method for ^{90}Sr determination using ^{85}Sr labelled carrier*

(*Received* 25 *April* 1960)

^{90}Sr is usually determined by β-counting of ^{90}Y milked off from a previously purified ^{90}Sr–^{90}Y equilibrium solution containing only strontium and yttrium carriers. The strontium carrier yield in the purification steps is subsequently determined gravimetrically by precipitation of strontium carbonate or oxalate from the residual solution.[1]

In natural materials, especially soils and dairy products, this method involves a separation of milligram amounts of strontium from large quantities of calcium. The most commonly adopted procedure is the fractional precipitation of strontium nitrate from strong nitric acid solutions.[2,3] This procedure is tedious and time consuming. Strontium yields and decontamination factors are strongly dependent on the Ca/Sr ratio as well as on calcium and nitric acid concentrations.[4]

A new method, based on using ^{85}Sr—spiked strontium carrier solution is proposed. The ^{85}Sr γ-activity enables a direct determination of the strontium carrier recovery, thus obviating the need for chemical isolation of strontium. This activity does not interfere with the assay of ^{90}Sr which is carried out, as usual, by β-counting of the separated ^{90}Y fraction. The radiochemical procedure is designed to eliminate any interfering fission product activity from the final ^{90}Y sample. This is achieved by conventional scavenging procedures, the most important of which involves the carrying of any such activity on a subsequently discarded $Y(OH)_3$ precipitate, prior to ^{90}Y growth in and milking. Possible contamination by ^{140}La, grown in simultaneously with the ^{90}Y, is eliminated by the previous removal of its parent ^{140}Ba on a $BaCrO_4$ precipitate. The same procedure, of course, reduces γ-emitting contamination of the strontium containing solution to levels negligible in comparison with the amount of ^{85}Sr introduced. It is not claimed, however, that sufficient decontamination for direct β-counting of this fraction is guaranteed by the procedure.

The method consists of the following steps.

The sample is brought into solution and a suitable amount of strontium carrier, spiked with ^{85}Sr, is added. A mixed carbonate precipitate is carried down and ignited to remove organic material. The residue is dissolved in acid and purified by a $Fe(OH)_3$ scavenge followed by a $BaCrO_4$ scavenge, carbonate precipitation and finally $Y(OH)_3$ scavenge. The residual solution is acidified and diluted to constant volume after adding a known amount of yttrium carrier. The γ-count of an aliquot of this solution is compared to that of the original strontium carrier. After a two weeks equilibration period, yttrium is milked off from the solution by a double yttrium hydroxide precipitation, followed by dissolution and reprecipitation as yttrium oxalate which is mounted and β-counted. The radiochemical purity is checked by taking a decay curve. The yttrium carrier recovery is determined by ignition of the sample and weighing as Y_2O_3.

The ^{90}Sr content of the sample is computed using the following formula:

$$^{90}\text{Sr dis/min per unit weight} = \frac{A \cdot G_i \cdot e^{\lambda_Y t}}{w \cdot \alpha \cdot G_f \cdot E \cdot y}$$

* The work was performed as part of an investigation by the author in partial fulfillment of the requirements for a Ph.D. Thesis.

(1) L. E. Glendenin, *Radiochemical Studies, The Fission Products* Vol. 3, N.N.E.S., Paper 236. McGraw-Hill, New York (1951).
(2) F. J. Bryant, A. C. Chamberlain, H. Morgan and G. S. Spicer, Harwell Report AERE HP/R 2056 (1956).
(3) J. H. Harley and I. B. Whitney, U.S.A.E.C. Report NYO 4700 (1957).
(4) J. Gat, E. Rappaport and I. Teucher, Israel A.E.C. Report, IA 516 (1959).

A = the ^{90}Y β-count in counts/min,

G_i = the γ-count of the initial carrier solution in counts/min,

G_f = the γ-count of the sample aliquot in counts/min,

α = a dilution factor, taking into account the dilution of carrier in sample,

E = overall efficiency of the counter,

y = fractional Y carrier recovery,

w = weight of sample,

$e^{\lambda_Y t}$ = decay correction factor, λ_Y being the ^{90}Y decay constant (0·011 h^{-1}) and t the time interval between the yttrium separation and counting.

The overall standard deviation (based on 1 per cent accuracy in γ-counting, 1–5 per cent accuracy in β-counting, $\frac{1}{2}$ hr uncertainty in t and 2 per cent in y) is 3–6 per cent. The method was applied to the analysis of two local soils using an ammonium acetate (pH 7) leaching procedure.[5] Five-hundred gramme samples were used. As a comparison same soils were also analysed using the conventional nitric acid strontium calcium separation subsequent to leaching, as well as at the Health and Safety Laboratory, New York by the courtesy of Dr. J. H. HARLEY.

About 20 mμc of ^{85}Sr (supplied by ORNL) were employed for each sample. The γ-counts were performed in a NaI well counter, and the β-samples were counted under a proportional gas flow end-window counter, of 47·5 per cent efficiency for ^{90}Y betas and about 15 counts/min background. The method was tested using ^{90}Sr standard (supplied by the Health and Safety Laboratory) in calcium containing solutions. The agreement between calculated and experimental results was well within statistical counting errors. The decay curves of the separated ^{90}Y showed no detectable contamination.

The results are summarized in Table 1.

TABLE 1

Sample number	Leachable calcium	Method of analysis	Sr carrier recovery (%)	^{90}Sr dis/min per kg	
1	4·2 g per kg soil	A	56	440 ± 40	A: new method
		B	43	465 ± 50	B: conventional method
		C		420 + 40	C: HASL (hydrochloric acid leach)
2	1·1 g per kg soil	A	85	93 ± 10	
		B	47	100 ± 20	
		C		41 ± 4	

The error indicated consists of average deviations in duplicate samples. The agreement is good, except for the large discrepancy between our and HASL results in sample no. 2. In view of the results on other samples from the same location our value seems to be more accurate,

The method appears to be a good alternative for the conventional fuming nitric acid separation in all cases where the simultaneous determination of ^{89}Sr by counting of the strontium precipitate is not required, although, under favourable conditions ^{89}Sr could be determined, using a counter of low γ-efficiency for direct β-counting of the Sr fraction. It can also be applied to other radioactive parent–daughter pairs where a suitable γ-emitting isotope of the parent element is available (such as ^{140}Ba—^{140}La, using ^{133}Ba).

Acknowledgement—The author wishes to thank Dr. J. R. GAT for valuable discussions, and Mrs. G. BARUCH for help with the analyses.

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[5] J. R. GAT and J. GILAT, to be published.

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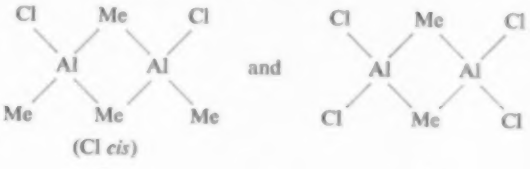
Concerning the structure of alkyl aluminium chlorides

(*Received* 11 *April* 1960; *in revised form* 23 *May* 1960)

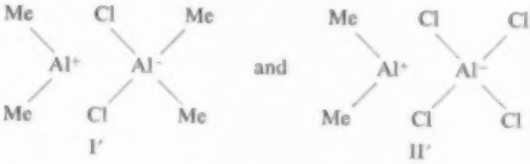
THE proton nuclear magnetic resonance spectra of methyl aluminium chlorides ($Al_2Me_nCl_{6-n}$; N = 2, 4, 6) have recently been published.[1,2] The compounds $Al_2Me_2Cl_4$ and $Al_2Me_4Cl_2$, individually in an inert solvent, show but one absorption separated by 0·3 p.p.m. At −60° (and at room temperature) a mixture of the two (25% $Al_2Me_2Cl_4$ in 75% $Al_2Me_4Cl_2$) exhibits but one resonance interpreted as indicating intermolecular methyl exchange even at −60°.[1,3] The NMR spectrum of Al_2Me_6 shows 2 lines at −75°, these lines coalescing into one at the weighted mean of the two with increasing temperature and thus indicating exchange of the two hypothecated types of methyl groups, bridging and end.[2]

The above interpretations for the chlorides[1] are derived from the assumed methyl-bridged structures postulated from Raman spectra,[4] (I) and (II).



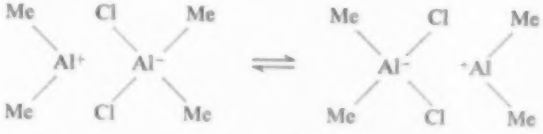
(Cl *cis*) I II

We wish to point out that the Raman results are compatible with the structures I′ and II′. (The tetrachloride has generally been assumed to have methyls asociated with both aluminium atoms as in II or as in I with the bridged methyls replaced by chlorines.)



I′ II′

For I′ then, magnetic equivalence of the methyl groups in the proposed structure for the dichloro compound can result from chloride exchange



The actual position of the resonance lines[5] are consistent with this postulation; the "end"-methyl frequency for the hexamethyl compound, +2·14 p.p.m., (from CH_2 in cyclohexane) more closely approximates the observed frequencies in the chlorides (1·75 p.p.m. dichloride; 1·45 p.p.m. tetrachloride) than does the "bridging"-methyl frequency, +1·07 p.p.m. In this analysis, no allowance is made for the electron withdrawing influence of the chloride; an effect which would be expected to reduce the observed frequencies when comparing hexamethyl with the chlorides.[3]

[1] S. BROWNSTEIN, B. C. SMITH, G. ERLICH and A. W. LAUBENGAYER, *J. Amer. Chem. Soc.* **82**, 1000 (1960).
[2] N. MULLER and D. E. PRITCHARD, *J. Amer. Chem. Soc.* **82**, 248 (1960).
[3] Not observing two peaks is not *a priori* evidence for exchange.
[4] C. P. VAN DER KELEN and M. A. HERMAN, *Bull. Soc. Chim. Belg.* **65**, 362 (1956). All structures, I, II, I′,II″, can be represented as tetrahedral aluminium atoms joined on an edge.
[5] B. P. DAILEY and J. N. SHOOLERY, *J. Amer. Chem. Soc.* **77**, 3977 (1955); M. P. GROENEWEGE, J. SMIDT and H. DE VRIES [*J. Amer. Chem. Soc.* **82**, 4426 (1960)] have extended the work cited in refs. 1 and 2 to investigations at lower temperatures and compared the results with those obtained on Ti alkyls. Their interpretation agrees in all respects with ours.

The structures involving methyl bridges are intuitively less satisfying than the halide-bridged structures. The ion pair structures are in accord with the Raman spectra, (i.e. symmetry for II′ C_{2v}; T_d), the numbers and polarizations of lines predicted agreeing with experiment quite as well as for the methyl-bridged structures but without the rather strange assumption that only the *cis* isomer (I) is found.[4] The time of observation for the Raman spectra, essentially the time for a vibration, is sufficiently short so that the structures observed correspond to the "ion-pair" structures, while the observation time for the NMR experiments is sufficiently longer so that the chloride exchange could cause but one line for the methyls. A mechanism for exchange of methyls in the mixture of I′ and II′ would be simple metathesis. Methyl exchange in hexamethyl could proceed through the equivocable ethane-like structure that was concluded from electron diffraction[6] on this substance. This "no electron bond" intermediate will be described further elsewhere.[7]

The chemistry of the alkyl aluminium compounds lends credence to the halide-bridged structures.[8] As the electron-donating character of the alkyl group decreases, the stabilities of the compounds decrease and conversely. A rather critical observation is that compounds $Al_2R_nCl_{6-n}$ are reported only for $n = 0, 2, 4, 6$; even in the hydrides polymerization occurs to the extent necessary for formation of AlR_2^+ units.[8]

The lack of compounds of $n = 1$, 3 and 5 can be reasonably ascribed to the processes

$$2Al_2MeCl_5 = Al_2Me_2Cl_4 + Al_2Cl_6$$

$$2Al_2Me_3Cl_3 = Al_2Me_4Cl_2 + Al_2Me_2Cl_4$$

$$2Al_2Me_5Cl = Al_2Me_4Cl_2 + Al_2Me_6$$

with the driving force for these reactions possibly derived from the stability of the $AlMe_2^+$ unit, and the stability conferred by double chloride bridges, except, of course, for the hexamethyl.

The only gas phase dipole moment measurement for the compounds $Al_2Me_nCl_{6-n}$ is for the tetrachloride: a dipole moment of 1·9 D was found, an impossible situation on the basis of the methyl-bridged structures but quite reasonable with halide bridges. Unfortunately, as the authors have indicated, the clarity of the result is not conducive to the drawing of firm inferences.[9]

The electron-diffraction results of BROCKWAY and DAVIDSON[6] favour the halide-bridged structures, although here too, equivocation is possible. The totality of the evidence seems more compatible with the halide-bridged structures than with the methyl bridged structures.

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[6] L. O. BROCKWAY and N. R. DAVIDSON, *J. Amer. Chem. Soc.* **63**, 3287 (1941).
[7] A. ZWICKEL and R. E. GLICK, to be published.
[8] G. E. COATES, *Organo-Metallic Compounds* p. 7288. Methuen, London (1956).
[9] R. H. WISWALL and C. P. SMYTH, *J. Chem. Phys.* **9**, 352 (1941).

Some studies in the inorganic chemistry of the reaction between uranyl fluoride and chlorine trifluoride

(*Received* 25 *May* 1960)

THE fluorination of uranium tetrafluoride with chlorine trifluoride to yield uranium hexafluoride has been discussed by LABATON[1]. Another process by which uranium hexafluoride may be made involves the treatment of uranyl fluoride with chlorine trifluoride, and an attempt has been made to define the inorganic chemistry of the reaction by establishing the nature of the gaseous products.

[1] V. Y. LABATON, *J. Inorg. Nucl. Chem.* **10**, 86 (1959).

Experimental

Chemicals

Uranyl fluoride used in all experiments was prepared by the interaction of uranium hexafluoride with steam. The water content of the material as prepared was approximately 0·6 wt. %, corresponding with an approximate formula $UO_2F_2.0{\cdot}1H_2O$. Determination of surface area by the B.E.T. method[1] using nitrogen as adsorbate gave a value of 12·2 m^2/g.

Commercial chlorine trifluoride was freed from impurities by redistillation, and its purity checked by gas chromatography.

Apparatus

The apparatus was a modification of that of ELLIS *et al.*[2], adapted to include a reaction vessel adjoining the sample volume (see Fig. 1). The reaction vessel was a 5 in. length of 1 in. i.d. nickel pipe,

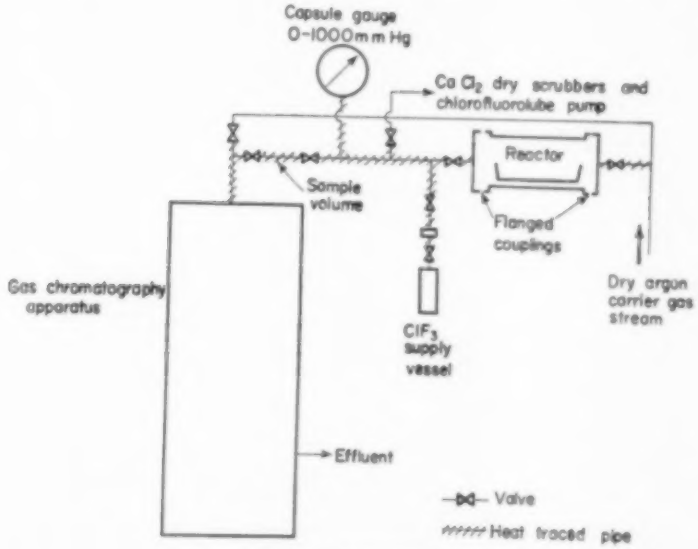

FIG. 1.—Apparatus.

mounted horizontally, into which a nickel boat containing uranyl fluoride could be loaded. The reaction vessel was fitted into the apparatus with flanged couplings sealed with copper joint rings of diamond cross-section. Heat was supplied to the apparatus using tape heaters controlled by a variable-voltage transformer.

The gas chromatographic unit was identical with that described by ELLIS *et al.*[2] using the 11 ft 6 in. column packed with a 50 wt. % loading of Kel-F grade '10' oil (Kellogg Corp., Jersey City, U.S.A.) on ground polytetrafluoroethylene powder sieved to 30–60 B.S. mesh; argon was used as carrier gas and a Martin gas density balance acted as detector. Calibration curves were recorded for oxygen (retention time referred to peak maximum-2·0 min at carrier flow rate 27·5 cm^3/min), chlorine monofluoride (2·7 min), hydrogen fluoride (3·4 min), perchloryl fluoride (ClO_3F) (4·7 min), chlorine (5·7 min), chloryl fluoride (ClO_2F) (6·8 min), chlorine trifluoride (8·3 min) and uranium hexafluoride (37·5 min). Perchloryl fluoride and chloryl fluoride were prepared by reaction of potassium chlorate with fluorine and chlorine trifluoride, respectively, as described by ENGLEBRECHT and ATZWANGER[4], and purified by redistillation.

[1] S. BRUNAUER, P. H. EMMETT and E. TELLER, *J. Amer. Chem. Soc.* **60**, 309 (1938).
[2] J. F. ELLIS, C. W. FORREST and P. L. ALLEN, *Analyt. Chim. Acta* **22**, 27 (1960).
[4] A. ENGLEBRECHT and H. ATZWANGER, *J. Inorg. Nucl. Chem.* **2**, 348 (1956).

Procedure

In each run 1·0 g of uranyl fluoride was spread evenly over the base of the nickel boat, the couplings of the reaction tube were remade and the tube was evacuated. After degassing for 2 hr at 100°C to remove any free water, the reaction vessel was allowed to attain a desired temperature, and batches (about 0·25 g) of chlorine trifluoride at 300 mm Hg pressure were introduced. After allowing time for complete reaction, the resultant gases were allowed to expand into the evacuated sample volume, which was isolated. After the pressure had been measured, and surplus gas pumped away, the sample containing product gases was immediately passed to the gas chromatographic unit and analysed.

Results

The reaction was investigated at three temperatures: 150, 100 and 50°C. At 150 and 100°C, with reaction times of 10 min, the whole of each batch of chlorine trifluoride reacted, with the exception of the final two or three batches in each case, when only a small amount of unreacted chlorine trifluoride was recovered. At 50°C only about half the chlorine trifluoride was profitably used after 30 min reaction time, and the final batches in each run needed some hours to react completely. In run 5 the average reaction time was 30 min, increasing to 60 min in run 6 and 90 min in run 7.

A summary of the reaction products from interaction of uranyl fluoride with chlorine trifluoride at various temperatures is given in Table 1. Results have been converted to molar equivalents.

TABLE 1.—PRODUCTS OF ClF_3–UO_2F_2 REACTION

Run	Temp. (°C)	Total contact time (hr)	Reactants, molar equivalents		Gaseous products, molar equivalents					
			UO_2F_2	ClF_3	UF_6	O_2	Cl_2	ClF	ClO_2F	ClO_2
1	150	1¾	1·0	1·87	1·0	0·49	0·49	0·46	0·40	–
2	150	1¾	1·0	1·97	1·0	0·37	0·43	0·47	0·47	–
3	100	2	1·0	1·94	1·0	0·12	0·16	1·02	0·59	–
4	100	2	1·0	2·01	1·0	0·11	0·17	1·00	0·57	–
5	50	25	1·0	2·16	1·0	0·04	0·04	1·56	0·51	0·20
6	50	27	1·0	2·22	1·0	0·01	0·03	1·61	0·60	0·04
7	50	32	1·0	2·70	1·0	0·03	0·04	1·78	0·55	–

All the compounds quoted in Table 1 were positively identified, with the exception of chlorine dioxide: this substance is the most probable cause of a distorted peak at 8·0 min retention time (cf. above) overlapping the ClF_3 peak in elution traces. A specimen of chlorine dioxide was prepared and shown to elute at 8·0 min, but tended to decompose somewhat on the column. The figures quoted for this material in Table 1 are very approximate. The figure given for chlorine trifluoride was obtained by subtracting the amount recovered from the total admitted to the reaction vessel. On balancing the elements admitted and recovered, there is an over-all deficiency in recovery of all elements except uranium. This is shown in Table 2, in which the mean stoicheiometry of the ClF_3–UO_2F_2 reaction is summarized.

Discussion and Conclusions

Most of the over-all fluorine loss is undoubtedly caused by reaction of the initial chlorine trifluoride batches with the unfluorinated walls of the reaction vessel, to produce nickel fluoride. This has been identified by X-ray crystallographic examination of scrapings from the reaction vessel walls. A further loss is caused by reaction of chlorine trifluoride with residual water in the uranyl fluoride; this yields hydrogen fluoride which is mostly adsorbed on the vessel walls, though traces have been recorded in the first batch analysis of some runs. The relatively high amount of unaccountable fluorine at the lowest temperature may well be a result of the increased contact times involved.

The discrepancy in the chlorine balance is not particularly serious in any case, and is negligible at the lower temperatures. The 5 per cent loss at 150°C is probably caused by the formation of metal chloride as well as fluoride in wall reactions.

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TABLE 2.—MEAN STOICHEIOMETRY OF THE ClF_3–UO_2F_2 REACTION

Temp. (°C)	Reactants, molar equivalents		Products, molar equivalents						Unaccountable, equivalents		
	UO_2F_2	ClF_3	UF_6	O_2	Cl_2	ClF	ClO_2F	ClO_2	O_2	F	Cl
150	1·0	1·92	1·0	0·43	0·46	0·46	0·44	–	0·13	0·86	0·10
100	1·0	1·98	1·0	0·12	0·17	1·01	0·58	–	0·30	0·35	0·05
50	1·0	2·36	1·0	0·03	0·04	1·65	0·55	0·08	0·36	0·88	–

The over-all deficiency in oxygen is more difficult to account for. At 50°C the balance is worst in run 7 when the longest reaction times were permitted and no chlorine dioxide was recorded. Further, the nearest approach to a balance is in run 5 where reaction times were shorter and a relatively large amount of chlorine dioxide appeared to be present. As the reaction temperature increased, no chlorine dioxide was noted, and the oxygen balance improved. It seems possible, therefore, that chlorine dioxide may form in the early stages of the reaction and subsequently dissociate, most rapidly at higher temperatures. Whilst it exists it is possible that oxidation of the apparatus occurs, resulting in a deficiency of volatile oxygen compounds recovered (cf. the strong oxidizing power of chlorine dioxide mentioned by MELLOR[5]).

This study shows that uranyl fluoride may be completely converted to uranium hexafluoride by treatment with chlorine trifluoride at temperatures from 50 to 150°C. The other gaseous reaction products are oxygen, chlorine, chlorine monofluoride and chloryl fluoride, with the possibility of chlorine dioxide as a reaction intermediate. The relative amounts of these products vary with the reaction temperature. At 150°C the stoicheiometry of the reaction may be reasonably expressed by:

$$2UO_2F_2 + 4ClF_3 \rightarrow 2UF_6 + Cl_2 + ClF + ClO_2F + O_2 + \underset{\text{Lost to reaction vessel}}{(F_2)}$$

Molecular oxygen and chlorine in appreciable quantities only result at the higher temperatures in the range considered. There is an increasing tendency for chlorine monofluoride to be produced at the lower reaction temperatures, with a corresponding fall in chlorine production. This is probably caused by secondary reaction of chlorine monofluoride with uranyl fluoride at the higher temperatures. Amounts of chloryl fluoride vary little with reaction temperature. A kinetic study of the reaction is being pursued by Kennedy *et al.*[6] These authors have shown that the initial reaction of residual water of hydration in uranyl fluoride with chlorine trifluoride is very rapid compared with the subsequent process producing uranium hexafluoride. The strongly exothermic reaction with residual water creates local high temperatures which enhance the rate of the chlorine trifluoride–uranyl fluoride reaction at its outset.

Though it is generally seen that a temperature in excess of 100°C is required to complete the reaction relatively rapidly, it is evident that the interpretation of results and the assignation of stoicheiometrical equations is complicated by side reactions of the reactive halogen gases both with residual water in the uranyl fluoride (which is most difficult to dehydrate beyond $UO_2F_2.0{\cdot}1H_2O$) and with the walls of the reaction vessel.

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The preparation of anhydrous plutonium trichloride

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PLUTONIUM trichloride was first produced by direct combination of the elements at 450°C and 60 mm pressure.[1] Various other methods of preparation involving gas-solid reactions have been described by GARNER *et al.*[2] and ABRAHAM *et al.*[3] These methods include the use of phosgene or hydrogen chloride-hydrogen mixtures as chlorinating agents. All the methods are very time consuming when gram quantities of plutonium are involved. We report results on the chlorination of plutonium dioxide, plutonium (III) "carbonate" and plutonium (III) and (IV) oxalates by either phosgene or by hydrogen chloride.

Experimental

Plutonium (III) and (IV) oxalates were precipitated by the addition of oxalic acid solution to a solution of plutonium (IV) in nitric acid or of plutonium (III) in either nitric acid or hydrochloric acid. The precipitates were washed with dilute acid, filtered on to a sintered glass frit and "air-dried". Plutonium (III) "carbonate" was precipitated by the addition of excess solid ammonium carbonate to a solution of plutonium (III) in hydrochloric acid. Plutonium dioxide was prepared by the ignition in air of plutonium sulphate, $Pu(SO_4)_2$, at 800°C in a muffle furnace.

The results on the 0·5 g Pu scale were obtained using a simple tube furnace. The other results were obtained using a furnace assembly designed to agitate the solid reactants continuously by rotation of the furnace tube at 2 rev/min in an attempt to reduce the effect of the depth of the bed on the rate of chlorination. Dry hydrogen chloride or phosgene was fed into the furnace tube through a rotating seal. The contents of the reaction tube were always kept within a hot zone of uniform temperature maintained to within ±20°C of the desired temperature.

For the hydrochlorination experiments the material to be hydrochlorinated was heated for a predetermined time at 140°C in the furnace tube in a stream of argon. The hydrogen chloride was then introduced and the temperature increased to the final operating temperature over a period of about 15 min. After a given time at the operating temperature the products were allowed to cool in a current of argon. Any condensate found at the end of the furnace tube was removed with a micro-pipette and the end of the tube was dried with paper tissue. The product was then quickly tipped out into a plastic weighing bottle and stored in a desiccator.

When using phosgene the procedure was slightly different, thus: (1) the starting materials had already been heated at 140–200°C for 2 hr before introduction into the furnace tube and (2) the phosgene was introduced at the start of the run and the temperature was then raised.

The products reported in Table 1 were not analysed, but experience had shown that a reliable test for the purity of the plutonium trichloride was its solubility in water since the starting solids and any impurities in the product were insoluble in water. The product was considered to be 100 per cent plutonium trichloride when it dissolved in water to give a blue solution completely free of turbidity. All other products were analysed for plutonium, chlorine and oxalate content. Plutonium was determined by α-counting, and spectrophotometrically as plutonium (III). Oxalate was determined by titration with standard permanganate and the lower limit that could be detected represented about 0·3 per cent oxalate in the product. Chloride was determined by the Volhard method.

Results

(a) *Chlorination by phosgene*

(i) *The chlorination of plutonium dioxide.* No reaction took place below 700°C (cf. BUDAYER and VOLSKY[4]); small samples (10–50 mg) were rapidly and completely chlorinated at 850°C but larger (5 g) samples were only partly chlorinated since a layer of molten plutonium trichloride prevented the

[1] F. HAGEMANN, Metallurgical Project Report USAEC Document CK-1327 (1944).
[2] S. E. BAKES, C. S. GARNER, I. B. JOHNS, G. H. MOULTON and B. WEINSTOCK, USAEC Document LA. 112 (1944).
[3] B. M. ABRAHAM, B. B. BRODY, N. R. DAVIDSON, F. HAGEMANN, I. KARLE, J. J. KATZ and M. J. WOLF, *Preparation and Properties of Plutonium Chlorides and Oxychlorides*. NNES, Div. IV, Vol. 14B, Paper 6,7. McGraw-Hill, New York (1949).
[4] I. V. BUDAYER and A. N. VOLSKY. *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Vol. 28, Paper 2195. United Nations (1959).

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reaction going to completion. At 1200°C the plutonium trichloride was quantitatively volatilized but was difficult to condense efficiently and the $PuCl_3$ "smoke" produced when the temperature of the carrier gas fell below about 600°C was also difficult to trap.

(ii) *The chlorination of plutonium* (III) *"carbonate" and oxalate by phosgene.* Complete conversion of the plutonium (III) oxalate to plutonium trichloride (on the 0·5 g Pu scale) was obtained in 3–4 hr at 600–650°C but the product was contaminated with carbon. The results of the chlorination of plutonium (III) "carbonate" with phosgene are given in Table 1. Quantitative conversion of the "carbonate" to the trichloride has been repeatedly obtained on the 20 g Pu scale.

TABLE 1.—CHLORINATION OF Pu (III) "CARBONATE" WITH PHOSGENE

Run no.	Scale (g)	Duration of experiment (hr)	Temperature (°C)	Flow rate of phosgene (l/hr).	Conversion to $PuCl_3$
1	0·5	1·75	350	1–3	Incomplete
2	0·5	0·85	400	1–3	Complete
3	0·5	1·25	400	1–3	Complete
4	0·5	2·25	400	1–3	Complete
5	0·5	2·75	500	2–5	Almost complete
6	0·5	3·75	500	1–3	Complete
7	3·0	5·25	500	2–5	Complete
8	5·0	10·25	500	2–5	Complete
9	0·5	3·25	550	2–5	Almost complete
10	1·0	3·25	550	2–5	Complete
11	0·5	3·75	700	2–5	Almost complete
12	20·0	8	500–550	2–5	Complete

(b) *The hydrochlorination of plutonium* (III) *or* (IV) *oxalate*

It was found desirable to heat the oxalates at 140°C (in argon) for 1–2 hr before introducing hydrogen chloride at 140°C. The results of runs in which the time of hydrochlorination was varied are given in Table 2. Unless otherwise stated the oxalates were heated for 2 hr at 140°C in a stream of argon before hydrochlorination.

TABLE 2.—THE EFFECT OF TIME OF HYDROCHLORINATION ON THE PERCENTAGE OF CHLORINE IN THE PRODUCT (FOR $PuCl_3$; Cl = 30·7%)

Time of hydrochlorination at 140–500°C (hr)	1	2	3	4
Cl in the product (%)	27·0	29·9	28·2	30·0
	26·7	28·7[a]	28·5[a]	29·9
		28·1[a]		30·7
				30·2
				25·3[b]

[a] 1 hr heating at 140°C
[b] product contained 20% of PuOCl

The time taken to increase the furnace temperature from 140 to 500°C (with hydrogen chloride flowing) was varied from 15 min to 210 min and, for a fixed total time of hydrochlorination (4 hr), it was found preferable to increase the temperature quickly (140–500°C in 15 min). Light brown powders containing very little chlorine were obtained when hydrogen chloride was not introduced until the temperature had reached 500°C and it is desirable to introduce the hydrogen chloride at 140°C.

With plutonium (III) oxalate, the rate of hydrochlorination at 200°C was exceedingly slow but quantitative conversion to plutonium trichloride was possible in 4 hr at 500°C. Temperatures in the range 400–550°C were used with plutonium (IV) oxalate and the optimum temperature was 500°C. The rate of hydrochlorination was considerably slower at 400° while at 550°C brown powders of low chlorine content were obtained.

Discussion

The nature of the intermediates produced during the thermal decomposition of Pu(IV) or Pu(III) oxalates is unknown, but DAWSON[5] has found that no stable carbonate is formed and the characteristic X-ray pattern of PuO_2 does not appear below 400°C on ignition of $Pu(C_2O_4)_2 6H_2O$ in air. The thermogravimetric decomposition curve[6] of Pu(III) oxalate in air does not indicate the presence of any stable intermediate between $Pu(C_2O_4)_3$ and PuO_2.

In a study of the thermal decomposition of thorium oxalate, D'EYE and SELLMAN[7] found that the product (ThO_2) was contaminated with carbon which they suggested was formed by the disproportionation of the carbon monoxide produced by the decomposition of the oxalate. The carbon formed during the chlorination of Pu(III) oxalate by phosgene may be formed by a similar reaction. Carbon monoxide is also formed in the dissociation of phosgene: $COCl_2 \rightleftharpoons CO + Cl_2$, and at 400–500°C the equilibrium lies well over to the right hand side of the equation. In our experiments it is unlikely that thermal equilibrium was reached.

In the production of $PuCl_3$ by the action of hydrogen chloride on $Pu(C_2O_4)_2 6H_2O$, a reducing agent is necessary unless $PuCl_4$ is formed as an intermediate. This is unlikely, since all attempts to prepare $PuCl_4$ have been unsuccessful.[8] The thermal decomposition of hydrogen chloride is very small at 500°C ($\ll 10^{-3}$ per cent dissociation) and the reducing agent may be the carbon monoxide formed on decomposition of the plutonium oxalates.

The composition of the plutonium (III) "carbonate" used in our work is not known but it may well be a mixture of ammonium plutonium carbonates similar to those found by GEL'MAN and ZAITSEV[9] in the case of PuIV "carbonate".

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The extraction of uranyl nitrate by tributyl phosphate in the presence of some nitrate salting-out agents

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THE extraction of uranyl nitrate from nitric acid solution by tributyl phosphate (TBP) was reported in a previous paper.[1,2] The salting-out effect of some nitrates upon the extraction of uranyl nitrate by TBP was investigated in the present work.

[1] T. SATO, *J. Inorg. Nucl. Chem.* **6**, 334 (1958).
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Aqueous phases containing uranyl nitrate of 5 g/l. and varying nitric acid concentrations were extracted with 19 per cent TBP in kerosene using various nitrate salting-out agents at 20°C in the manner described in the earlier paper.[1] Uranium was determined gravimetrically after separation[3,4] from other metals.

The percentage of uranyl nitrate extracted[1] was determined at various nitric acid concentrations in the presence of nitrate salting-out agents at 1 M concentration. The results are given in Table 1

TABLE 1.—EXTRACTION OF URANYL NITRATE USING VARIOUS NITRATE SALTING-OUT AGENTS

Nitrate salting-out agents	Percentage extracted			
	0 M*	1 M*	3 M*	6 M*
(HNO_3)	2·96	82·10	95·52	97·10
NH_4NO_3	70·00	92·30	96·50	97·40
$LiNO_3$	73·05	94·60	97·50	97·95
$NaNO_3$	72·50	93·00	97·10	97·80
KNO_3	65·00	90·50	96·00	97·10
$Cu(NO_3)_2$	86·02	97·50	97·70	99·00
$Mg(NO_3)_2$	84·35	97·20	97·50	99·40
$Ca(NO_3)_2$	82·48	96·60	96·60	97·50
$Zn(NO_3)_2$	79·75	98·05	98·10	99·40
$Al(NO_3)_3$	99·90	99·60	98·20	99·50
$Fe(NO_3)_3$	99·80	99·50	98·20	98·90

* This expresses the initial aqueous nitric acid concentration.

In Table 1 it is seen that although the presence of nitrate salting-out agents favours the extraction of uranyl nitrate, its effect is most remarkable at low acidities. And the percentage extracted of uranyl nitrate with trivalent metal nitrate at zero HNO_3 *viz-a-viz* that at 3 M HNO_3 concentration increases

TABLE 2.—AMOUNT OF NITRATE SALTING-OUT AGENTS CO-EXTRACTED DURING THE EXTRACTION OF URANYL NITRATE

Nitrate salting-out agents	Percentage co-extracted	
	0 M*	1 M*
$LiNO_3$	—	—
$NaNO_3$	—	—
KNO_3	—	—
$Cu(NO_3)_2$	0·050	0·025
$Mg(NO_3)_2$	—	—
$Ca(NO_3)_2$	0·118	0·064
$Zn(NO_3)_2$	0·005	—
$Al(NO_3)_3$	0·004	0·003
$Fe(NO_3)_3$	0·010	0·008

* This expresses the initial aqueous nitric acid concentration.

[3] U.S.A.E.C. Report A-2919, Vol. 1 (1946).
[4] C. J. RODDEN, (Editor-in-Chief), *Analytical Chemistry of the Manhattan Project*. McGraw-Hill, New York (1950).

slightly. The present author has shown in a previous paper[1] dealing with uranyl nitrate extraction vs. nitric acid concentration that the extraction of uranyl nitrate is a maximum at 6 M HNO_3; it may be that at low acidity this maximum is displaced to lower nitrate ion concentration, and the shape of the extraction vs. nitrate ion concentration curve is altered when, comparatively, the nitrate complexing of the uranium is increased and nitric acid competition for the available TBP is reduced.[5]

The amount of nitrate salting-out agents co-extracted with uranyl nitrate into TBP is shown in Table 2.

From Table 2 it is observed that small amounts of some nitrate salting-out agents (Cu, Ca, Zn, Al and Fe) are co-extracted with uranyl nitrate into the organic phase at low acidities. But the order of the percentage co-extracted of the nitrates is different from that of their solubilities[6] into TBP.

The effect of the amount of nitrate salting-out agents is presented in Fig. 1.

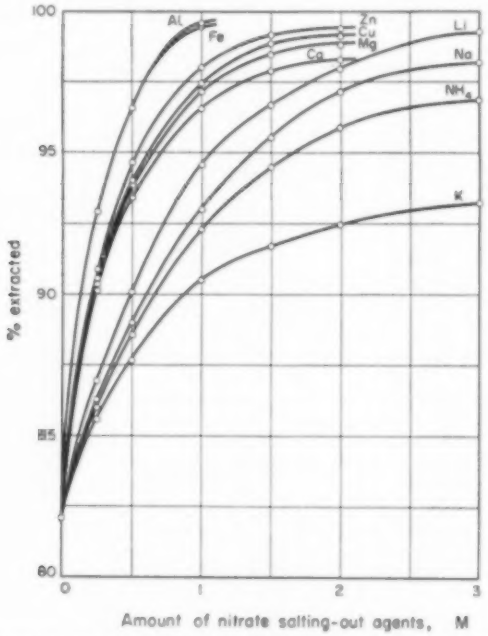

FIG. 1.—Effect of amount of nitrate salting-out agents upon the extraction of uranyl nitrate at 1 M initial nitric acid concentration.

In Fig. 1 the salting-out effect of nitrates decreases in the order of Al, Fe, Li, Zn, Cu, Mg, Na, Ca, NH_4 and K at 4 M (1 M HNO_3 plus an amount of nitrate). Although the order of the salting-out effect of monovalent nitrates corresponds to the order of their activity coefficients, that of bivalent metal nitrates does not always correspond to the order of their activity coefficients.[7]

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A new method for the conversion of inorganic salts to the corresponding perchlorates

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NITROSYL perchlorate was found to react with inorganic salts, the anions of which form volatile nitrosyl compounds, to yield the solid, anhydrous metal perchlorates. This displacement reaction is believed to be of interest because it represents a new synthetic method of introducing the perchlorate group and possibly provides a relatively simple method of preparing various volatile nitrosyl compounds. In the experiments following, the salts KNO_3, KCl, NaF, $Ba(NO_3)_2$, and AgBr were reacted with nitrosyl perchlorate to give substantial conversions of the former materials to the corresponding perchlorates by the general, overall reaction:

$$MX_n \text{ (solid)} + nNOClO_4 \text{ (solid)} \rightarrow nNOX \text{ (gas)} + M(ClO_4)_n \text{ (solid)} \quad (1)$$

The reported reaction[1] between silver perchlorate and nitrosyl chloride in a sealed tube producing silver chloride and nitrosyl perchlorate would appear to indicate that the displacement reactions of nitrosyl perchlorate might be of an equilibrium nature. Accordingly, in the present studies, reaction (1) was driven to the right by removal of the volatile reaction products from the reaction site.

Experimental Procedures and Results

The preparation of and analytical methods applied to nitrosyl perchlorate have been described in detail elsewhere.[2] (Chlorine: Found, 27·28%: Calc. for $NOClO_4$, 27·39%. Nitrosyl group: Found, 23·16%: Calc. for $NOClO_4$, 23·17%.) The additional salts used were all of reagent grade and were treated by drying at 110° for 12 hr prior to use.

The reaction mixtures (0·8 to 1·2 g) of Table 1 were prepared by mixing the components under anhydrous conditions. After standing for 24 hr in a tube vented through a drying tube filled with magnesium perchlorate, the resultant samples were heated at 50°, 75° and 100° for 4 hr periods at atmospheric pressure with venting of the gaseous reaction products; the samples were then heated under vacuum (3–5 mm Hg) for 3 hr, ground, and reheated under vacuum for 12 hr at 100°. Heating of the mixtures under vacuum conditions provided a convenient means for removing volatile nitrosyl compounds. Nitrosyl perchlorate itself undergoes thermal decomposition to gaseous products at elevated temperatures.[2,3,4] The results of chemical analyses of the final products are given in Table 1. Nitrosyl perchlorate was determined by reaction with excess sodium hydroxide solution and back-titration with standard acid.[2] Total chlorine was found by precipitation as silver chloride after fusion of the sample with sodium carbonate in a platinum crucible. Except for mixture (b), chlorine as chloride or chlorate was not present in any of the reaction residues.

In the instances of mixtures (a), (b) and (c), considerable reaction, as measured by weight losses, was noted to have occurred after standing at ambient temperature for 24 hr. Thus, 1·0138 g of (a) lost 0·1650 g; 0·7845 g of (b) lost 0·0691 g and 1·2456 g of (c) lost 0·0618 g. In an additional experiment 1·8549 g of a mixture containing 49·96 wt. % KNO_3 and 50·04 wt. % $NOClO_4$ underwent a weight loss of 0·1833 g after standing for one week in a vented tube at room temperature; 1·0004 g of nitrosyl perchlorate under similar conditions showed no change in weight after a three week period.

Discussion

Though pure metal perchlorates were not obtained in these studies, it is likely that prolongation of the reaction times at the lower temperatures, repeated grinding between heating periods, and longer evacuation intervals would have resulted in final products of greater purity.

The displacement behavior of nitrosyl perchlorate appears to be an example of a more general type

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TABLE 1.—SUMMARY OF RESULTS

Sample (MX_n)	Mole ratio $\frac{NOClO_4}{MX_n}$	$NOClO_4$ (wt. %)	Residue composition			
			$NOClO_4$ (wt. %)	MX_n (wt. %)	Cl (wt. %)	$M(ClO_4)_n$ (wt. %)
a (KNO_3)	1·852	70·33	6·85	2·02 (by diff.)	25·20	91·13
b (KCl)	0·946	62·15	1·80	1·14	25·54 (calc., 25·60	97·06 (by diff.)
c (KCl)	1·711	74·82	10·73	0·00	25·61 (calc., 25·79)	89·27 (by diff.)
d (NaF)	1·873	85·24	11·29	16·85 (by diff.)	23·90	71·86
e ($Ba(NO_3)_2$)	3·700	64·70	13·04	46·70 (by diff.)	11·85	39·26*
f (AgBr)	1·990	57·85	2·67 (by diff.)	3·77	—	93·56†

* Found 39·35%: Calc. Ba content of residue 40·58%.
† Based on water-soluble Ag content of 48·68%.

of reaction which may be characteristic of ionic or highly polar nitrosyl compounds. A number of examples involving other nitrosyl compounds are to be found in the literature:

$$NOBF_4 + NaF \rightarrow NOF - NaBF_4{}^{(5)} \quad (2)$$

$$NOHSO_4 + NaCl \rightarrow NOCl - NaHSO_4{}^{(6)} \quad (3)$$

$$NOCl + AgF \rightarrow NOF - AgCl{}^{(7)} \quad (4)$$

Nitrosation reactions in general:[8,9] $Aryl{:}H - NO^+ \rightarrow Aryl:NO + H^+$ (5)

The nitrosyl perchlorate reactions described here bear a formal analogy to those displacement reactions involving condensed phases as reported by HEDVALL[10,11] to occur between metal oxides and metal salts (e.g. $MO - M'X \rightarrow MX - M'O$, where $X = CO_3$, SO_4, SiO_3, Cl or S). The negative values for the free energy changes of these reactions are due primarily to their exothermic nature. The nitrosyl perchlorate reactions, however, have been computed to be endothermic[12] and must proceed because of favourable entropy changes.

Acknowledgement—The studies reported herein were conceived during fulfillment of work performed by New York University for Picatinny Arsenal under Contract DAI-30-069-501-ORD-(P)-1549.

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LETTERS TO THE EDITOR

Preparation, structure and electrical properties of some substituted lithium-oxo-metallates

(*Received* 8 *July* 1960)

We would like to report the preparation of two series of substituted ternary oxides of the types $LiMe_{0.5}Me'_{0.5}O_2$ and $Li_2Me_{0.5}Me'_{0.5}O_3$, where Me = Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2} and Me′ = Ti^{+4}, Mn^{+4}, Nb^{+5}, Ta^{+5}. These compounds may be derived from the unsubstituted compounds $LiFe^{+3}O_2$ and $Li_2Ti^{+4}O_3$, which are known to crystallize in a random sodium chloride structure. The lattice parameters and some electrical properties of the new compounds are summarized in Table 1.

TABLE 1.—LATTICE PARAMETERS AND ELECTRICAL PROPERTIES OF THE SUBSTITUTED LITHIUM-OXO-METALLATES

No.	Composition	a_0 (Å)	Resistivity (Ω cm)	Dielectric constant	Seebeck coefficient (μV/deg^{-1}*)
1	$LiMn_{0.5}Ti_{0.5}O_2$	4·216	$>2\cdot10^9$	14·7	—
2	$LiFe_{0.5}Ti_{0.5}O_2$	4·137	$3\cdot10^4$	—	+295 (186°C)
3	$LiCo_{0.5}Ti_{0.5}O_2$	4·166	$>2\cdot10^9$	14·8	—
4	$LiNi_{0.5}Ti_{0.5}O_2$	4·144	$>2\cdot10^9$	11·3	—
5	$LiFe_{0.5}Mn_{0.5}O_2$	4·184	$>3\cdot10^9$	70·1	—
6	$LiCo_{0.5}Mn_{0.5}O_2$	4·150	$8\cdot10^3$	—	−59·6 (262°C)
7	$LiNi_{0.5}Mn_{0.5}O_2$	4·137	$6\cdot10^4$	—	−75·1 (265°C)
8	$Li_2Mn_{0.5}Nb_{0.5}O_x$	4·211	$>7\cdot10^9$	16·5	—
9	$Li_2Fe_{0.5}Nb_{0.5}O_x$	4·192	$>2\cdot10^9$	18·5	—
10	$Li_2Co_{0.5}Nb_{0.5}O_x$	4·184	$9\cdot10^5$	—	−274 (273°C)
11	$Li_2Ni_{0.5}Nb_{0.5}O_x$	4·184	$3\cdot10^4$	—	−35 (250°C)
12	$Li_2Cu_{0.5}Nb_{0.5}O_{2.75}$	4·214	$9\cdot10^4$	—	+75 (188°C)
13	$Li_2Zn_{0.5}Nb_{0.5}O_{2.75}$	4·213	$>5\cdot10^9$	18·5	—
14	$Li_2Mn_{0.5}Ta_{0.5}O_x$	4·212	$>5\cdot10^9$	12·5	—
15	$Li_2Fe_{0.5}Ta_{0.5}O_3$	4·192	$>2\cdot10^9$	10·9	—
16	$Li_2Co_{0.5}Ta_{0.5}O_x$	4·174	$2\cdot10^5$	—	−470 (250°C)
17	$Li_2Ni_{0.5}Ta_{0.5}O_x$	4·184	$1\cdot10^5$	—	−61·5 (285°C)
18	$Li_2Zn_{0.5}Ta_{0.5}O_3$	4·214	$>6\cdot10^9$	25·0	—
19	$LiZn_{0.5}Ti_{0.5}O_2$	a_0 = 13·90 c_0 = 6·19	$>4\cdot10^8$	13·7	—

* The mean temperature for the measurement is given in parentheses.

In general, the compounds were prepared by stoicheiometric interaction of the corresponding oxide components either in air, when all metals were in their maximum valence state, or under purified argon, if lower valent oxides were used. It was possible to substitute ions as large as Zn^{+2} and still retain the cubic structure for the $Li_2Me_{0.5}Me'_{0.5}O_3$ type; however, $LiZn_{0.5}Ti_{0.5}O_2$ was not cubic. This compound was indexed on the basis of a tetragonal structure.

The compounds with oxygen ratios marked x were of particular interest with regard to stoichiometry because of a possible oxygen-deficient structure. If the nickel in $Li_2Ni_{0.5}Nb_{0.5}O_x$ were bivalent

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the formula would be $Li_2Ni_{0.5}Nb_{0.5}O_{2.75}$, whereas tervalent nickel would result in the full co-ordination of $Li_2Ni_{0.5}Nb_{0.5}O_2$. To distinguish between these possibilities, magnetic susceptibility measurements were carried out by Dr. R. B. HAND of this Laboratory for $Li_2Ni_{0.5}Ta_{0.5}O_x$ and $Li_2Ni_{0.5}Nb_{0.5}O_x$. A susceptibility of 3·56 Bohr magnetons was found for the first, and 3·34 for the latter compound, which may be compared to the theoretical moments of 3·88 for Ni^{+3} and 2·83 for Ni^{+2}. It appears therefore that in these compounds the nickel exhibits an intermediate valence state. This conclusion is further supported by the fact that a distinct phase width for the parameters can be detected as a function of the oxygen content, as shown by the following values:

$Li_2Ta_{0.5}Ni_{0.5}O_x$ prepared in air; $a_0 = 4{\cdot}1844$ Å

$Li_2Ta_{0.5}Ni_{0.5}O_x$ prepared in argon; $a_0 = 4{\cdot}1884$ Å

With the exception of $LiFe_{0.5}Ti_{0.5}O_2$ and $Li_2Cu_{0.5}Nb_{0.5}O_{2.75}$ the conducting oxides are *p*-type semiconductors.

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Preparation of long-lived terbium-157 and terbium-158*†

(*Received* 12 *July* 1960)

PREVIOUS investigations of the unstable terbium isotopes having mass 157 and 158 have revealed that the mass-157 nuclide has a half-life of less than 10 min or greater than 25 years[1] while a 111 keV magnetic octupole transition has been attributed to the de-excitation of an isomeric state of the odd-odd 158 nuclide.[2,3] Nuclear spectroscopic investigations indicate that the nuclear ground state of terbium-157 has spin 3/2[4] in accordance with the unified nuclear model,[5] which, in addition, predicts even (positive) parity for this ground state. Investigations using paramagnetic resonance and optical spectroscopy have revealed that stable gadolinium-157 also has nuclear spin 3/2,[6,7] while odd (negative) parity is indicated by the unified nuclear model. The ground state of terbium-158 may be described by assigning the odd proton to the 3/2+ orbital indicated for terbium-157 and the odd neutron to the $3/2^-$ orbital for gadolinium-157. The two states with spins and parities 0- and 3- that arise from these orbitals satisfactorily account for the isomerism observed. On this basis the β-decays of both the terbium-157 and terbium-158 ground states to low-lying states of the respective product nuclei are expected to be at least first-forbidden. Additionally, low energies are expected for these β-decay processes, since both terbium nuclides lie close to stability; thus it appears reasonable that these isotopes have long lifetimes and have previously remained unobserved.

In the continuation of a programme to identify and study long-lived isotopes in the rare earth region,[8] a 5 mg sample of dysprosium oxide enriched to 13·8 per cent in the mass-156 isotope has been irradiated with neutrons in the Materials Testing Reactor. The sample, contained in a quartz ampoule, received an exposure of 2×10^{21} neutrons/cm² over a 3 month interval. Four months after irradiation, mass analysis of the unseparated sample was made by using a 30 cm radius solid-sample

* Work done under the auspices of the U.S. Atomic Energy Commission.

† A portion of this work is taken from a thesis submitted by J. L. Power to Princeton University in partial fulfilment of the requirements for the Ph.D. Degree.

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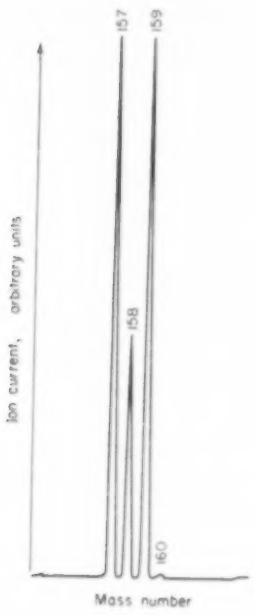

FIG. 1.

mass spectrometer. The presence of mass peaks at 157, 159, 165 and 166, unobservable in the sample before irradiation, indicated neutron capture in dysprosium-156, -158 and -164. The sample was next chemically fractionated by cation-exchange chromatography to yield pure fractions of the various rare earth elements. The holmium, dysprosium and terbium fractions were identified by scintillation spectroscopy, which revealed the presence of holmium-166, dysprosium-159 and terbium-160. Mass-spectrometric investigation of the terbium fraction revealed the existence of mass peaks at 157, 158, 159 and 160, indicating the preparation of new long-lived isotopes terbium-157 and -158 in addition to the stable terbium-159 and 76-day terbium-160. The relatively high abundance of terbium-158 produced by the neutron capture of terbium-157 points to a high cross-section for this process.

A lower limit for the K-capture half-life of both terbium-157 and terbium-158 may be set by observing that the isotopic ratios of terbium-157 and -158 to terbium-160 are approximately 160 and 70, respectively, and also that the K X-ray and γ-ray spectrum of the terbium fraction is predominantly that of 76-day terbium-160. Assuming that the K radiation due to K-capture of terbium-157 and terbium-158 is less than the K radiation accompanying the decay of terbium-160 (primarily due to the high K conversion of the 84-kV transition in gadolinium-160), we conclude the K-capture half-lives of these isotopes are greater than 30 years and 15 years respectively. These isotopes will be further examined to search for evidence of electron-capture processes and to determine pertinent neutron cross-sections.

It is a pleasure to acknowledge the cooperation of the staff of the Materials Testing Reactor in carrying out the irradiation.

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The composition of "OPPA"

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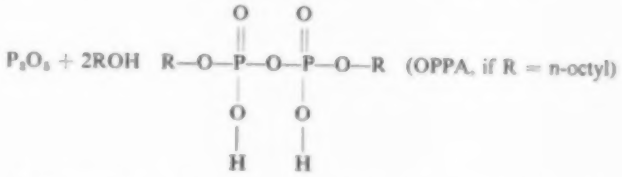
In a number of recently published papers concerning "OPPA" (e.g.[1,2]), use is made of a reaction formulated as



as published by Long *et al.*[3] Calculations are made involving the complexes between "OPPA" (regarded as a single compound) and uranium.

However, it is known from the work of Cherbuliez[4] that, the phosphorus pentoxide molecule being a P_4O_{10} tetrahedron with 6 P—O—P bonds, incomplete alcoholysis must yield a mixture of alkyl *ortho*-, *pyro*- and *meta*-phosphates.

In this laboratory, a comparison was made of uranium extraction from phosphoric acid by "OPPA" and by pure dioctyl pyrophosphoric acid as obtained by the synthesis starting from $POCl_3$.[5] "OPPA" was found more effective by two orders of magnitude.

Fig. 1.—Paper chromatography of "OPPA".

[1] D. Grdenic and B. Korpar, *J. Inorg. Nucl. Chem.* **12**, 149 (1959).
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That "OPPA" is a mixture was proved by paper chromatography:

A drop of "OPPA" solution in kerosene, containing 30–50 μg P, was submitted to ascending alkaline chromatography, the solvent being n-propanol 40%; isobutanol 15%; water 40%; ammonium hydroxide 5%(w/w). Optimum separation was obtained after 16 hr and at 10°C. The chromatogram was then sprayed with a perchloric-molybdic acid reagent and made visible by reduction with H_2S.

This chromatographic procedure yielded seven spots, indicating a mixture of seven components. (Fig. 1).

These results were further corroborated by analysis for P—O—P bonds by titration. This showed that only part of the phosphorus participates in these bonds.

Also, the infra-red spectrum of "OPPA" as compared to the spectrum of the pure dioctylpyrophosphoric acid showed wider bands, while the OH band was missing.

Work is now being done on the identification of the components of "OPPA".

Acknowledgement—The author thanks Dr. Y. MARCUS for helpful discussion of this letter.

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A list of some of the papers to be published in future issues

L. B. ASPREY and T. K. KEENAN: Tetravalent lanthanides—I. Sodium praseodymium fluorides.

D. BANERJEA and K. K. TRIPATHI: Association of uranium(VI) with anions in aqueous perchloric acid medium.

M. LEFORT et X. TARRAGO: Importance et rôle du radical NH_2 dansla décomposition de l'hydroxylamine par les rayonnements ionisants en solution aqueuse.

G. W. A. FOWLES and D. NICHOLLS: Hexahalogenotitanates.

R. E. ENRIONE and R. SCHAEFFER: Interconversion of boranes—II. Deuterium isotope effect in the decomposition of diborane.

M. H. KURBATOV and C. W. TOWNLEY: Isolation of carrier free rhodium from ruthenium targets.

D. F. PEPPARD, G. W. MASON and I. HUCHER: Acidic esters of phosphonic acid as selective extractants for metallic cations. Selected MIII tracer studies.

H. SMALL: Gel-liquid extraction. The extraction and separation of some metal salts using tri-n-butyl phosphate gels

D. COHEN: Electrochemical studies of plutonium ions in perchloric acid solution.

T. R. SATO and H. H. STRAIN: Heat produced upon neutron irradiation of containers of various materials and its effect upon the neutron activation products of disodium phosphate.

S. KONGPRICHA and A. F. CLIFFORD: The hydrogen fluoride solvent system—V. The thermodynamic solubility product constant of CaF_2 and the basicity of water in liquid HF.

K. W. LOACH and T. A. TURNEY: The acetone complex of nitroprusside ion.

J. E. DRAKE and G. W. A. FOWLES: Hexachlorozirconates.

A. K. HOLLIDAY and A. G. MASSEY: The reaction of diborane tetrachloride with some simple π-bonded molecules

M. BAAZ, V. GUTMAN und L. HÜBNER: Der Nachweis von Chloridionenübergängen in Phosphorxychloridlösungen durch bildung des $[FeCl_4]^-$-ions aus $FeCl_3$.

N. S. GILL, R. H. NUTTALL, D. E. SCAIFE and D. W. A. SHARP: The infra-red spectra of pyridine complexes and pyridinium salts.

E. L. SHORT and D. F. C. MORRIS: Zinc chloride and zinc bromide complexes—I. Cation exchange studies with zinc-65 tracer.

T. J. COLLOPY and J. J. KLINGENBERG: Spectral evidence for zirconium–mandelic acid complexes in ethanol

C. J. BARTON and R. A. STREHLOW: Phase relations in the systems LiF–PuF_3.

A. S. WILSON and W. E. KEDER: The extraction of uranium(IV) from nitric acid by tri-n-octylamine.

M. M. BENARIE: Enrichment of the ^{6}Li-isotope in dekagram quantities by electromigration in molten lithium chloride.

N. S. GILL and R. S. NYHOLM: The structure of bis-pyridine metal dihalide complexes.

P. A. D. DE MAINE and G. E. MCALONIE: Inorganic salts dissolved in non-aqueous or in mixed solvents—VII.

P. A. D. DE MAINE and E. J. WALSH: Inorganic salts dissolved in non-aqueous or in mixed solvents—X.

F. E. SAALFELD and H. J. SVEC: The mass spectrum of stannane.

H. R. HOEKSTRA and S. SIEGEL: The uranium–oxygen system: U_3O_8–UO_3.

J. O. WEAR, C. V. MCNULLY and E. S. AMIS: A study of transference and solvation phenomena—III. Lithium chloride in water–ethanol and ethanol solvents.

E. BLASIUS und K. D. BECCU: Untersuchung des Kontaktaustausches von ionenaustauschern unter Zuhilfenahme von Radionukliden.

J. FUGER: Actinide and lanthanide ion exchange separation studies. Separations by aminopolyacetic acids—II.

A. GLASNER and M. STEINBERG: The thermal decomposition of lanthrum oxalate.

M. FRENI and V. VALENTI: Rhenium co-ordination compounds.

I. REZANKA, J. FRANA, M. VOBECKY and A. MASTALKA: Radioactive decay of ^{49}Sc.

D. J. MACDONALD and C. S. GARDNER: Kinetics of aquation of *trans*-dichlorobis (ethylenediamine) chromium(III) cation.

J. D. FARR, A. L. GIORGI, M. G. BOWMAN and R. K. MONEY: The crystal structure of actinium metal and actinium hydride.

R. KENT MURMANN: The rate of oxygen exchange between ReO_4^- and H_2O.

S. LA PLACA, I. BINDER and B. POST: Binary dodecaborides.

H. W. KIRBY: Calorimetric determination of the half-life of protactinium-231.

R. W. HOFF, J. M. HOLLANDER and M. C. MICHEL: The neutron-deficient chain ^{80}Sr–^{80}Rb.

D. COHEN: The absorption spectra of plutonium ions in perchloric acid solutions.

E. L. MUETTERTIES and J. E. CASTLE: Reactions of hydrogen fluoride with metals and metalloids.

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IMPORTANCE ET RÔLE DU RADICAL NH_2 DANS LA DÉCOMPOSITION DE L'HYDROXYLAMINE PAR LES RAYONNEMENTS IONISANTS EN SOLUTION AQUEUSE

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Abstract—In the course of a general study of the physico-chemical effects of radiation on different compounds of nitrogen in aqueous solution, we were interested particularly in the behaviour of hydroxylamine and in the properties of the radical NH_2, the existence of which appears to be well established. It was possible to determine exactly the stages of the oxidation–reduction mechanisms from hydroxylamine to ammonia (reduction of NH_2OH) and from hydroxylamine to nitrogen and various oxides (oxidation of NH_2OH) by deeper study of the effects of high-energy radiation on aqueous solutions. One of us has published these results in entirety elsewhere, but it is interesting to note here that this study provides a means of elucidating the mechanism of certain chemical processes and, in particular, of obtaining completely original information about the effect of the radical NH_2 on the dissociation of $NH_3^+ \rightleftarrows NH_2 + H^+$.

In addition we have calculated the complete kinetics of the decomposition of hydroxylamine under radiation.

Résumé—Au cours d'une étude générale sur les effets physicochimiques des rayonnements sur différents composés de l'azote en solution aqueuse, nous nous sommes plus particulièrement intéressés au comportement de l'hydroxylamine et aux propriétés du radical NH_2 dont l'existence semble bien établie. Il a été possible de préciser les étapes des mécanismes d'oxydo-réduction conduisant de l'hydroxylamine à l'ammoniaque (réduction de NH_2OH) ou au contraire de l'hydroxylamine à l'azote et aux divers oxydes (oxydation de NH_2OH) grâce à l'étude approfondie des effets des rayonnements de grande énergie sur les solutions aqueuses. Les résultats complets de ces effets ont été exposés par ailleurs par l'un de nous,[1] mais il est intéressant de noter ici que cette étude fournit un moyen d'élucider le mécanisme de certains processus chimiques et notamment d'apporter des renseignements entièrement originaux sur la nature du radical NH_2 sur la dissociation de $NH_3^+ \rightleftarrows NH_2 + H^+$.

On a en outre calculé la cinétique complète de la décomposition de l'hydroxylamine sous rayonnement.

1. *Rappel de quelques proprietes caracteristiques de l'hydroxylamine*

L'hydroxylamine résulte de la substitution d'un atome H de l'ammoniac par un radical oxhydrile. Cette substitution diminue le caractère basique du produit obtenu. Au point de vue oxydo-réduction, l'atome d'azote dans l'hydroxylamine correspond á un état intermédiaire entre l'hydrazine et l'azote moléculaire. Comme l'ammoniaque, l'hydroxylamine donne des produits d'addition ou de coordination et des dérivés de substitution.

La molécule d'hydroxylamine n'est pas plane. Le radical oxhydrile se trouve dans le plan bissecteur des deux atomes H. Les longueurs de liaisons NH sont très voisines de celles dans NH_3. Dans l'ion hydroxylamonium NH_3OH^+, l'azote porte la charge positive. Il est á un sommet d'un tétrahèdre dont les autres sommets sont les atomes

[1] X. TARRAGO, *Ann. Chim.* (*Sér.* A) 3367 (1960).

d'hydrogène. Le radical oxhydrile se trouve dans la direction opposée à ce tétrahèdre.

Mais la caractéristique essentielle de l'hydroxylamine et de ses sels en solution aqueuse provient de leur possibilité de jouer un rôle tantôt oxydant tantôt réducteur, en raison même de la transformation en composés plus réduits (NH_4OH ou N_2H_4) ou plus oxydés (N_2, N_2O et oxydes d'azotes). La vitesse et le terme de l'oxydation sont d'ailleurs fonction de la concentration en NH_2OH. Ainsi par exemple nous avons constaté que dans une solution 5×10^{-3} M en sulfate d'hydroxylamine (pH = 4·4), l'action de l'eau oxygénée est lente et conduit en parties égales à l'azote et oxyde azoteux, alors que pour une concentration plus élevée, divers auteurs ont indiqué qu'il se forme de l'acide nitrique et qu'à 40°C la transformation en milieu acide est quantitative.[2]

Les potentiels d'oxydo-réduction* de l'hydroxylamine par rapport aux autres composés de l'azote ont été calculé.[3,4] Par rapport à l'azote, l'ammoniaque et $N_2O_2H_2$:

$$N_2 + 2H_2O + 4H^+ + 2e \rightleftarrows 2NH_3OH^+ \qquad E_0 = -1{\cdot}87 \text{ V}$$
$$NH_3OH^+ + 2H^+ + 2e^- \rightleftarrows H_2O + NH_4^+ \qquad E_0 = +1{\cdot}35 \text{ V}$$
$$N_2O_2H_2 + 6H^+ + 4e^- \rightleftarrows 2NH_3OH^+ \qquad E_0 = +0{\cdot}496 \text{ V}$$

L'hydroxylamine libre est caractérisée également par son instabilité. Sa décomposition est favorisée en milieu alcalin et par une élévation de température. Elle correspond à une dismutation dont l'équation globale s'écrit en milieu neutre ou alcalin:

$$3NH_2OH \rightarrow N_2 + NH_3 + 3H_2O + 3 \times 57 \text{ kcal}$$

En milieu acide on est conduit au résultat suivant:

$$4NH_2OH \rightarrow N_2O + {}_2NH_3 + 3H_2O + 4 \times 45{\cdot}2 \text{ kcal}$$

Les sels sont cependant plus stables que la base libre. Le mécanisme de ces décompositions n'est pas élucidé mais il est très probable que le radical NH_2 est un intermédiaire important.

Les solutions aqueuses d'hydroxylamine sont légèrement conductrices de l'électricité. On écrit habituellement par analogie avec l'ion NH_4^+.

$$NH_2OH + H_2O \rightarrow NH_3(OH)_2 \qquad -3{\cdot}8 \text{ kcal}$$

$$NH_3(OH)_2 \rightleftarrows NH_3OH^+ + OH^- \qquad k = 6{\cdot}6 \times 10^{-8}$$

ce qui conduit à adopter[4] une énergie libre de formation $\Delta F^\circ = 13{\cdot}54$ kcal pour l'ion hydroxylamonium NH_3OH^+. Cet ion peut donc être considéré comme un acide faible de $pK_A = 6$.

L'énergie libre de formation de l'hydroxylamine en solution aqueuse est faible: $\Delta F^\circ = 5{\cdot}60$ kcal, ce qui rend compte de son instabilité et de la facilité avec laquelle elle se transforme en ammoniaque. Par ailleurs cela rend possible de nombreuses réactions comme nous le verrons ultérieurement.

Nous avons travaillé avec des solutions aqueuses de sulfate d'hydroxylamine. Pour une concentration de 5×10^{-3} M on obtient un pH compris entre 4·3 et 4·4. En raison du pK de 6, on peut calculer que 99·5 per cent de l'hydroxylamine est à ce

* Convention de signe: potentiels croissants vers les milieux plus oxydants.

[2] BARRETT, *Proc. Chem. Soc.* **26**, 233 (1910).
[3] G. CHARLOT, D. BEZIER et J. COURTOT, *Potentiels d'Oxydo-réduction*. Pergamon Press, London (1958).
[4] W. M. LATIMER, *Oxidation Potentials*. Prentice-Hall, New York (1952).

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pH entièrement sous forme ionique NH_3OH^+. On a également fait une partie de cette étude à pH 6 par addition de soude aux solutions aqueuses de sulfate d'hydroxylamine. Ces solutions sont tamponnées à ce pH par l'hydroxylamine elle-même puisque son pK est de six.

2. *Caracteristiques de l'action du rayonnement sur les solutions d'hydroxylamine. Radicaux libres.*

Le mécanisme de l'action des rayonnements gamma sur l'eau est assez bien connu* et peut être schématisé brièvement en trois étapes:

(1) cession d'énergie aux molécules d'eau sous forme d'ionisations et d'excitations localisées le long des trajectoires.
(2) transformation des ions positifs en radicaux libres oxhydriles et des électrons en atomes d'hydrogène et peut-être en hydrogène moléculaire.
(3) diffusion et réactions de ces espèces radicalaires. Au début de cette diffusion, la concentration en radicaux est assez grande pour que les réactions entre eux produisent de l'eau oxygénée et de l'hydrogène moléculaire, la compétition avec les réactions sur les corps dissous étant négligeable.

Du point de vue des réactions chimiques et particulièrement des réactions d'oxydoréduction susceptibles d'être ainsi produites sur un corps dissous, seule la dernière étape nous préoccupe ici. On à l'habitude de l'exprimer quantitativement en indiquant le nombre de chacunes des espèces produites par unité d'énergie absorbée dans l'eau. Le rendement correspond donc au nombre de radicaux OH, H ou de molécules H_2 et H_2O_2 formés pour 100 eV d'énergie absorbée et se note G.
On peut écrire

$$G_{(-H_2O)} = G_{OH} + 2G_{H_2O_2} = G_H + 2G_{H_2}$$

La valeur du rendement effectif de radiolyse de l'eau en milieu neutre a été déterminée et se trouve voisine de 3·6. On verra d'ailleurs plus loin comment les solutions d'hydroxylamine nous ont permis de confirmer cette détermination.

Il nous faut maintenant envisager les réactions susceptibles d'être initiées sur l'hydroxylamine par les radicaux oxhydriles, l'hydrogène atomique et l'eau oxygénée, puis traiter leur cinétique pour rendre compte des résultats observés. Les résultats expérimentaux ont été exposés en détail par l'un de nous[1] et nous ne reviendrons pas sur leur descripiton complète. On donnera en appendice des indications sur l'analyse quantitative des principaux produits. Ils correspondent schématiquement à la dismutation de l'hydroxylamine en ammoniaque d'une part, azote et protoxyde d'azote de l'autre. La production de N_2O est négligeable à pH 6 et devient relativement importante à pH 4. En solutions plus acides (pH 2), le rendement de réduction de l'hydroxylamine est environ dix fois plus faible qu'à pH 6 et celui de formation d'ammoniaque est entièrement annulée. La courbe de variation de $G_{(NH3)}$ en fonction du pH est indiqué sur la Figure 1. On peut voir les points experimentaux obtenus soit par la mesure de rendement initiaux à divers pH donnés, soit par la mesure du rendement à une dose donnée qui correspond à un pH instantané mesuré. Ces dernières mesures sont extraites de courbes analogues à celles de la Figure 2. La précision a été déterminée par la méthode d'erreur quadratique moyenne sur un grand nombre de valeurs.

* On trouvera une mise au point toute récente sur cette question à la fin de l'ouvrage "Les radiations nucléaires".[2]

[1] M. LEFORT, *Les Radiations Nucléaires*. P.U.F., Paris (1959).

D'autre part, lorsqu'on porte la destruction d'hydroxylamine et la formation d'azote et de NH_3 pour une solution de pH initial 4·4, en fonction de la dose de rayonnement absorbée, on observe une incurvation prononcée vers l'axe des abscisses. Les rendements baissent donc très repidement comme on peut le voir sur la Figure 2.

Ce phénomène est concommitant à une baisse de pH. La transformation d'hydroxylamine en azote fait que les ions H SO_4^- du sulfate ne sont plus neutralisés par l'hydroxylamine et la formation d'ammoniaque n'est pas suffisante pour compenser

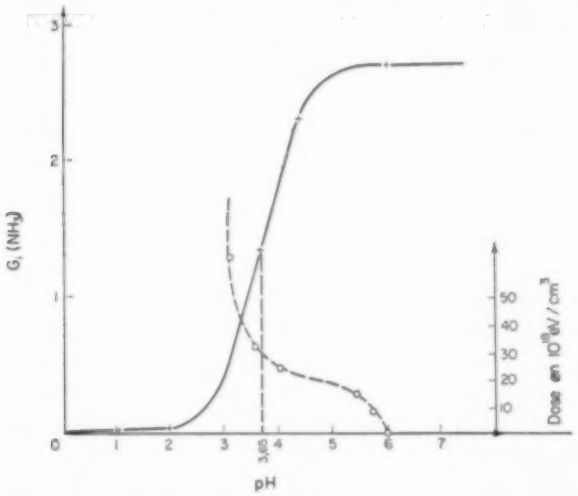

FIG. 1.—Irradiation aux rayons gamma de NH_3OH 5×10^{-3} M. Rendement de la formation de NH_4^+ en fonction du pH (+). La ligne en pointillés indique la variation du pH au cours de l'irradiation en fonction de la dose absorbée (abscisses de droite).

cet effet. Comme le rendement de radio-décomposition devient très rapidement faible lorsque le pH passe de 4·4 à 3, on est tenté d'expliquer par cet effet de pH l'incurvation des courbes.

Nous verrons plus loin que par un traitement cinétique quantitatif on peut rendre effectivement compte entièrement de la baisse de rendement par l'influence des ions H^+ sur le radical NH_2.

3. *Mecanisme et étapes de reactions*

Le grand rendement de décomposition de NH_3OH^+ à pH 4 à 6 et la formation simultanée d'ammoniaque et d'azote conduisent à penser que NH_3OH^+ est attaquée á la fois par les atomes H et par les radicaux OH. Nous avons fait l'hypothèse que la tendance pour OH était d'arracher un atome H et pour H un radical OH, de façon á reformer dans les deux cas une molécule d'eau avec une exothermicité importante.

$$NH_3OH^+ + OH \rightarrow NH_2OH^+ + H_2O \qquad (1)$$

$$NH_3OH^+ + H \rightarrow NH_4OH^+ \rightarrow H_2O + NH_3^+ \qquad (2)$$

$$NH_4OH^+ + OH^- \rightarrow NH_3OH + H_2O \qquad (2\text{ bis})$$

Ces deux réactions conduisent aux radicaux N $HOH(NH_2OH^+)$ et $NH_2(NH_3^+)$ dont nous devons examiner l'éventualité de la formation.

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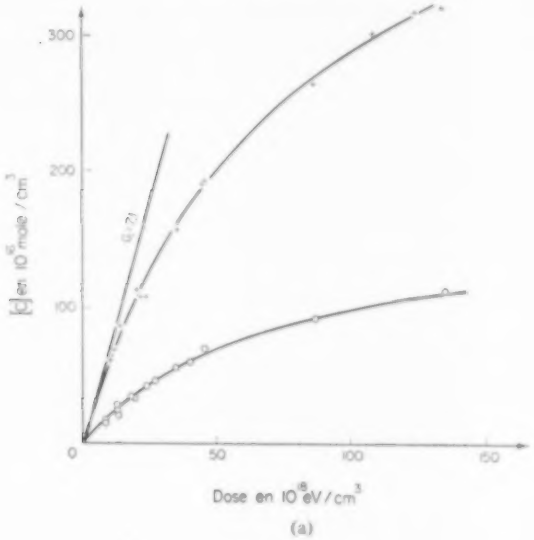
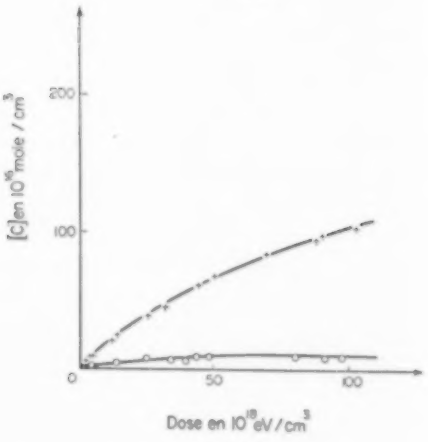


(a)



(b)

FIG. 2.—Irradiation d'hydroxylamine $5{\cdot}5 \times 10^{-3}$ M dans l'eau à pH 4·4. (a) mesure de l'hydroxylamine détruite + mesure de l'ammoniaque NH_4^+ ⊕. (b) Formation d'azote + Formation de N_2O ⊕.

(a) La variation d'énergie libre de la réaction (1) semble favorable. On a en effet avec les données récentes;[4]

$$\Delta F(1) = \Delta F(\text{NHOH}) + \Delta F(H_2O) - \Delta F(NH_2OH) - \Delta F(\text{OH})$$
$$= x - 56{\cdot}7 + 13{\cdot}6 - 8{\cdot}5 = x - 51{\cdot}6 \text{ kcal:}$$

Il faudrait que $x = \Delta F(\text{N HOH})$ soit supérieur à $+51{\cdot}6$ kcal pour que la réaction soit thermodynamiquement impossible.

Le radical N HOH* dont on suppose la formation par la réaction (1) conduit assez

* Nous remercions M. HAÏSSINSKY qui nous a suggéré d'ecrire l'intermédiaire monoazoto sous cette forme.

rapidement à l'azote moléculaire par dimérisation. Cependant le passage par un intermédiaire monoazoté semble indispensable. La structure exacte de ce composé est difficile à définir. ABEL[6] l'a introduit sous la forme N HOH dans un article relatif à l'autodécomposition de l'hydroxylamine. La dimérisation pourrait s'écrire après neutralisation de NH_2OH^+:

$$N\,HOH + N\,HOH \rightarrow [N_2H_2(OH)_2] \rightarrow N_2 + 2H_2O \qquad (3)$$

Comme seconde possibilité de réaction de N HOH on pourrait envisager son action sur l'hydroxylamine. Elle consisterait à enlever OH à NH_2OH.

$$N\,HOH + NH_2OH \rightarrow NH_2 + NOH + H_2O \qquad (3\text{ bis})$$

Elle n'est cependant guère envisageable car probablement endothermique puisqu' aussi bien NH_2 que NOH sont des radicaux instables. De plus on n'observe expérimentalement pas de N_2O produit de la dimérisation de NOH, à pH 6 et la réaction 4 bis conduirait à une chaine de destruction de l'hydroxylamine puisque NH_2 pourrait réagir selon (4). Une telle chaine n'a pas été observée.

TABLEAU I

	$-G(NH_2OH^+)$	$G(NH_4^+)$	$G(N_2)$	$G(N_2O)$	Bilan en N	$G(H_2O_2)$	$G(H_2)$
pH 6	7·9 ± 0·2	2·7 ± 0·05	2·7 ± 0·03	<0·1	8·1 ± 0·1	0·4 ± 0·1	0·42 ± 0·02
pH 4·4	7·1 ± 0·1	2·3 ± 0·05	2·0	0·40 ± 0·05	7·1 ± 0·2	0	0·42 ± 0·02
pH 2·0	0·80 ± 0·05	≤0·05	0·30 ± 0·03	0·10 ± 0·03	0·8 ± 0·12	0	
pH 0·5	0·80 ± 0·05	0	0·30 ± 0·03	0·10 ± 0·03	0·8 ± 0·12	0	0·47 ± 0·02

(b) Le radical NH_2 est connu en spectroscopie;[7] on l'a obtenu par irradiation ultraviolette de l'ammoniac et sa chaleur de formation a été calculée ($\Delta H_f = 41$ kcal/mol) par SZWARC[8]. On a déterminé par impact électronique[9] les valeurs de liaisons $NH_2^+ - H$ (119 kcal) et $NH_2 - H^+$ (172 kcal).

On peut calculer l'exothermicité des réactions (2) et (2bis) à partir de la valeur ΔH de NH_2 et en prenant 10 kcal pour ΔH(OH)

$$\Delta H(2) = \Delta H(NH_2) + \Delta H(H_2O) - \Delta H(OH) - \Delta H(NH_3OH^+)$$

$$= +41 - 68{\cdot}3 - 10 + 30 = -7 \text{ kcal.}$$

Cette réaction est donc exothermique.

Des considérations de structure et d'influence du pH nous ont amené à considérer le passage par le complexe NH_4OH^+ qui se décompose selon (2) ou (2 bis) d'après l'acidité du milieu.

En phase aqueuse on dispose de peu de renseignements mais il semble probable que le radical NH_2 puisse facilement enlever un atome d'hydrogène à l'hydroxylamine.

$$NH_3OH^+ + NH_2 \rightarrow NH_3 + NH_2OH^+ \rightarrow NH_4^+ + N\,HOH \qquad (4)$$

la transformation d'hydroxylamine en ammoniaque libérant beaucoup d'énergie ($E^\circ = 1{\cdot}35$ V).

Par les réactions (1) (2) (3) et (4), on est donc amené à la transformation de l'hydroxylamine en ammoniaque et azote.

[6] E. ABEL, *Monatsch.* **84**, 527 (1953).
[7] G. HERZBERG, D. A. RAMSAY. *Disc. Faraday Soc.* **14**, 11 (1953).
[8] M. SZWARC, *Quart. Rev.* **5**, 42 (1951).
[9] F. H. FIELD, J. L. FRANKLIN, *Electron Impact Phenomena* p. 349. Academic Press, New York (1957).

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(c) Outre les radicaux oxhydriles et l'hydrogène atomique, le rayonnement produit de l'eau oxygénée. Des expériences préliminaires nous avaient montré que H_2O_2 diluée ne réagit pratiquement pas sur les solutions 5×10^{-3} M d'hydroxylamine. Pour disparaître, l'eau oxygénée produite par la radiolyse de l'eau doit donc réagir sur un intermédiaire de la destruction de l'hydroxylamine. On peut envisager soit NH_2 soit N HOH. Des expériences complémentaires au cours desquelles on a irradié des mélanges d'eau oxygénée et d'hydroxylamine ont montré que les deux processus ont lieu, mais que le plus important et le plus rapide est celui de la réaction avec N HOH, NH_2 ayant déjà tendance à disparaître par réaction sur l'hydroxylamine. Cette action de H_2O_2 sur N HOH explique le formation de l'acide hypoazoteux $N_2O_2H_2$ à la façon du mécanisme de Fenton sur les ions ferreux:

$$NH_2OH^+ + H_2O_2 \rightarrow NOH + OH + H_3O^+ \qquad (5)$$

On peut évaluer ΔF (5) en appelant x et y les énergies libres de formation de NH_2OH^+ et NOH.

$$\begin{aligned}\Delta F(5) &= \Delta F(\mathrm{NOH}) + \Delta F(\mathrm{H_2O}) + \Delta F(\mathrm{OH}) - \Delta F(\mathrm{NH_2OH^+}) - \Delta F(\mathrm{H_2O_2}) \\ &= y - 56{\cdot}7 + 8{\cdot}5 - x + 31{\cdot}5 \\ &= y - x - 16{\cdot}7 \text{ kcal.}\end{aligned}$$

Si l'on admet que l'énergie libre de formation d'une structure moléculaire augmente avec l'instabilité on peut penser que $\Delta F(NH_2OH^+) = x > \Delta F(NOH) = y$, NOH étant plus stable que NH_2OH^+. Comme $y - x < 0$, on voit donc que

$$\Delta F(5) < -16{\cdot}7 \text{ kcal}$$

c'est á dire que la réaction (5) a lieu avec une variation d'énergie libre négative et se trouve possible thermodynamiquement.

Le radical OH ainsi formé attaque une nouvelle molécule d'hydroxylamine cependant que NOH, monomère connu de l'acide hypoazoteux peut réagir selon deux réactions dont l'importance relative dépend du pH:

$$NOH + NOH \rightleftarrows N_2O_2H_2 \rightarrow N_2O + H_2O \qquad (6)$$

$$NOH + NH_2OH \rightarrow N_2 + 2H_2O \qquad (7)$$

La réaction (7) est assez lente en milieu acide où la dimérisation (6) est favorisée comme l'indique l'observation de N_2O dans les produits de décomposition de l'hydroxylamine.

Le système de ces sept réactions permet de rendre compte des effets observés qui consistent essentiellement au grand rendement de décomposition d'hydroxylamine attaquée à la fois par OH, H et NH_2, à la formation comme produits principaux de NH_4^+ et d'azote par la réaction (4) et enfin à la production moins conséquente de N_2O. Il faut de plus ajouter la réaction de recombinaison (8)

$$H_2O + NH_3^+ + N\,HOH \rightarrow NH_3OH^+ + NH_2OH \qquad (8)$$

pour expliquer les faibles rendements, en milieu acide.

On a obtenu une confirmation de cette réaction en ajoutant de l'eau oxygénée qui réagit selon (5) avec N HOH. On rétablit alors un grand rendement en production d'azote car (8) est ainsi supprimée.

4. *Interpretation quantitative des resultats aux differents* pH

A partir des huit équations étudiées précédemment on a établi une cinétique permettant de calculer les rendements primaires de formation de radicaux OH, atomes H et eau oxygénée. On a habituellement recours en cinétique classique pour ce genre d'étude à la règle dite de "l'état stationnaire" qui consiste à écrire que la vitesse de formation de tous les intermédiaires instables est nulle. Cette règle n'est pas applicable strictement lorsque les intermédiaires sont produits par les rayons ionisants. En effet leur distribution n'est pas uniforme car leur formation succède à l'ionisation le long des rayons delta des trajectoires ionisantes. Cependant SCHWARZ et ALLEN[10] ont précisé une méthode équivalente à celle de l'état stationnaire mais qui n'implique pas une concentration uniforme. On considère non plus la *concentration* des intermédiaires mais *leur nombre*.

Supposons un intermédiaire X pouvant réagir selon une réaction (a)

$$A + X \rightarrow AX \quad (a)$$

ou (b)
$$B + X \rightarrow BX \quad (b)$$

La probabilité de réagir selon (a) est p_a et selon (b) p_b. On peut écrire:

$$\frac{p_a}{p_b} = \frac{k_a(X)\,(A)}{k_b(X)\,(B)}$$ ou k sont les constantes de vitesse.

$p_a + p_b = 1$ si les réactions (a) et (b) sont les deux seuls possibilites de disparition de X. On a donc

$$p_a = \frac{k(A)}{k_a(A) + k_b(B)}.$$

Ceci représente aussi la fraction des intermédiaires X qui disparaissent selon (a). Le nombre d'intermédiaire X formé par unité d'énergie absorbée (par exemple par 100 eV) est défini G_X. Si on représente par $G_{(a)}$ le nombre de fois où la réaction (a) a lieu par unité de dose et de volume, on a:

$$G_{(a)} = G_X \frac{k_a(A)}{k_a(A) + k_b(B)}$$

Reprenons maintenant les huit équations et examinons pour chaque valeur de pH à laquelle les expériences ont été faites à quelle cinétique nous sommes conduits:

(1) $NH_3OH^+ + OH \rightarrow NH_2OH^+ + H_2O \rightarrow N\,HOH + H^+ + H_2O$

(2) $NH_3OH^+ + H \rightarrow NH_4OH^+ \rightarrow NH_3^+ + H_2O$

(2 bis) $NH_4OH^+ + OH^- \rightarrow NH_3OH + H_2O$

(3) $N\,HOH + N\,HOH \rightarrow N_2H_2(OH)_2 \rightarrow N_2 + 2H_2O$

(4) $NH_3OH^+ + NH_2 \rightarrow NH_4^+ + N\,HOH$

(5) $NH_2OH^+ + H_2O_2 \rightarrow NOH + H_3O^+ + OH$

(6) $NOH + NOH \rightleftarrows N_2O_2H_2 \rightarrow N_2O + H_2O$

(7) $NOH + NH_3OH^+ \rightarrow N_2 + H_3O^+ + H_2O$

(8) $H_2O + NH_3^+ + N\,HOH \rightarrow NH_3OH^+ + NH_2OH$

[10] H. A. SCHWARZ et A. O. ALLEN, *J. Amer. Chem. Soc.* **77**, 1324 (1955).

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(A) pH 6–7 où le rendement est maximum il n'y a formation de N_2O qu'à l'état de traces. On sait par ailleurs que la réaction (6) n'a lieu qu'en milieu acide et on la négligera. $G(6) = 0$.

Le rendement en ammoniaque est maximum. Le partage de NH_4OH^+ entre (4) et (8) est donc entièrement déplacé vers (4). On suppose donc que NH_3^+ est en concentration très faible.

On observe la présence d'eau oxygénée dans les solutions irradiées de sorte qu'il faut supposer que la réaction (5) est lente et que seulement une partie de l'eau oxygénée produite par le rayonnement a réagi. Cela peut provenir d'une dissociation rapide à ce pH de NH_2OH^+ formé en (1), si bien que NHOH réagit selon (3). Avec la méthode définie précédemment on peut écrire une série d'équations.

$$G(NH_2) = G(2) - G(4) = 0$$

$$G_H - G(NH_4^+) = 0 \qquad G(NH_4^+) \text{ est mesuré} = 2{\cdot}7$$

$$G(N\,HOH) = G(1) + G(4) - 2G(3) - G(5) = 0$$

$$G(N_2) = \text{valeur mesurée de } 2{\cdot}7 = G(3) + G(7) = G(3) + G(5)$$

puisque $$G(NOH) = 0\; G(3) = 2{\cdot}7 - G(5)$$

$$G(1) = 5{\cdot}4 - G(5) - 2{\cdot}7 = 2{\cdot}7 - G(5)$$

D'autre part on a

$$G_{OH} + G(5) = G(1)$$

et le rendement primaire en eau oxygénée $G_{H_2O_2} = G(5) + G(H_2O_2)$; $G(H_2O_2)$ est la valeur mesurée de 0·4.

On obtient ainsi à partir des valeurs mesurées des rendements initiaux du Tableau 1 à pH 6

$$G_{OH} + 2G_{H_2O_2} = 3{\cdot}5 = G(-H_2O).$$

Comme on a mesuré par ailleurs le rendement en hydrogène $G(H_2) = G_{H_2} = 0{\cdot}42$, et que $G_H + 2G_{H_2} = G_{OH} + 2G_{H_2O_2} = 3{\cdot}5$ on en déduit $G_H = 2{\cdot}7$.

On retrouve la valeur directement mesurée par le rendement en ammoniaque.

Le rendement de décomposition de l'hydroxylamine s'écrit:

$$G(-NH_2OH) = 2G_H + G_{OH} + 2G_{H_2O_2} - 2G(H_2O_2) = 8{\cdot}1.$$

Les valeurs trouvées pour les rendements primaires sont en accord avec les déterminations les plus récentes obtenues avec d'autres systèmes.[11] En utilisant ces valeurs G_{OH}, G_H et $G_{H_2O_2}$ et les appliquant à notre schéma on trouverait donc par le calcul les rendements $G(NH_3)$, $G(N_2)$ et $G(-NH_2OH)$ que nous avons mesuré expérimentalement. Ceci nous semble être une indication en faveur du mécanisme supposé.

(B) pH 4·4. On remarquera qu'à plus faible pH, N_2O apparait aux dépens de l'eau oxygénée et que le rendement en NH_4^+ diminue de 2·7 à 2·3. Ces deux observations s'expliquent par l'intermédiaire des réactions (6) et (8). Il faut admettre en outre que la dissociation de NH_2OH^+ est plus lente qu'à pH 6, et que la réaction (5) a lieu aux dépens de (3).

[11] A. O. Allen et H. A. Schwarz, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Vol. 29, p. 30. United Nations (1958).

Comme précédemment on peut écrire un système d'équations qui, grâce aux mesures expérimentales portées dans le Tableau 1, conduit à déterminer

$$G_H = 2{\cdot}7 \quad G_{OH} = 2{\cdot}1 \qquad G_{H_2O_2} = 0{\cdot}75.$$

On peut également exprimer $G(8) = 0{\cdot}4$, $G(1) = 2{\cdot}85$ $G(4) = 2{\cdot}3$ $G(3) = 2{\cdot}0$ $G(5) = 0{\cdot}75$ et $G(7) = 0$

On se rend compte par exemple que les radicaux NH_2 sont partagés selon le rapport 2·3/0·4 entre les réactions (4) et (8) c'est à dire réagissent dans ce même rapport sous les formes NH_2 et NH_3^+.

(C) *Milieu acide.* Au fur et à mesure que le pH baisse, $G(8)$ augmente aux dépens de $G(4)$. Il en résulte une chute des rendements d'ammoniaque $G(NH_4^+) = G(4)$ et de destruction d'hydroxylamine $G(-NH_2OH) = G(1) + G(2) + G(4) - 2G(8)$. Lorsque la réaction (8) est totale, c'est à dire lorsque NH_2 est entièrement sous la forme NH_3^+, on obtient le mécanisme simplifié.*

$$NH_3OH^+ + OH \rightarrow N\,HOH + H_3O^+ \qquad (1)$$

$$NH_3OH^+ + H \rightarrow NH_3^+ + H_2O \qquad (2)$$

$$H_2O + NH_3^+ + N\,HOH \text{——} NH_3OH^+ + NH_2OH \qquad (8)$$

$$NH_3^+ + H_2O_2 \rightarrow N\,HOH + H_3O^+ \qquad (9)$$

$$N\,HOH + H_2O_2N \rightarrow OH + OH + H_2O \qquad (5)$$

5. *Dissociation de* NH_4OH^+, *effet du* pH *et cinetique de la formation de* NH_4^+

L'annulation du rendement en ammoniaque en solution acide est expliquée essentiellement par la compétition entre les réactions (4) et (8) et cette compétition dépend essentiellement de la forme sous laquelle se trouve le radical NH_2. On peut penser en effet que sous sa forme ionique NH_3^+, il ne peut réagir avec NH_3OH^+, en raison de la répulsion électrostatique des deux ions positifs. Comme la réaction (4) conduit à NH_4^+, on a vu que l'on pouvait calculer $G(4)$ et $G(8)$ et déterminer ainsi le rapport $G(4)/G(8)$ à divers pH. La courbe du rendement d'ammoniaque en fonction du pH a donc un point d'inflexion lorsque $G(4) = G(8)$. Ce point est voisin du pH 3·65.

En considérant que la variation des rendements initiaux en fonction du pH ne dépend que le la compétition entre les réactions (4) et (8), nous pouvons expliquer quantitativement les résultats expérimentaux obtenus.

Le rendement de la réaction (2) conduit aux radicaux NH_2 et NH_3^+ de sorte qu'on peut écrire:

$$G(2) = G_H = G(NH_4OH^+) = G(NH_2 + NH_3^+)$$

Comme tous les radicaux NH_2 conduisent à l'ammoniaque par la réaction (4), on peut écrire également:

$$G(NH_3) = G(NH_2)$$

On a défini G comme étant le rendement, c'est-à-dire la vitesse de formation pour un débit de dose par seconde donné D, $G = \frac{1}{D} \cdot \frac{d}{dt}$.

* Note: on trouvera une discussion plus détaillée de cet aspect dans la thèse de TARRAGO[1].

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On peut donc écrire encore:

$$G(NH_3) = \frac{d(NH_3)}{D\,dt} = \frac{d(NH_2)}{D\,dt} \qquad (I)$$

$\frac{d(NH_2)}{dt}$ étant la *vitesse de formation* du radical NH_2

De même $$G_H = \frac{d(NH_3)}{D\,dt} + \frac{d(NH_3^+)}{D\,dt} \qquad (II)$$

Examinons maintenant comment varie avec le pH la répartition entre NH_2 et NH_3^+ réagissant.

L'expérience nous a montré que cette répartition n'était pas modifiée par une variation de concentration en hydroxylamine et donc par la vitesse de la réaction (4). En effet, la production d'ammoniaque, entièrement due à cette réaction (4), n'est pas affectée lorsqu'on double ou triple (NH_3OH^+) à un pH fixé. On ne peut donc pas envisager une simple dissociation reversible de l'ion radical NH_3^+ en NH_2 et H^+, car l'augmentation de (NH_3OH^+) entraînerait un déplacement de l'équilibre vers NH_2. On doit admettre que les proportions de NH_3^+ et de NH_2(ou NH_3OH) sont établies de façon irréversible et dépendent du pH au moment de l'action des atomes H sur NH_3OH^+, selon (2).

Nous avons ainsi été amené à écrire la formation en un premier stade du composé NH_4OH^+, de structure vraisemblablement voisine de NH_4OH, qui se décomposerait normalement avec une constante de vitesse k_2 en NH_3^+ et H_2O. Cependant, en milieu neutre ou alcalin, la présence d'ions OH^- entraînerait la décomposition sous la forme (2bis).

$$NH_4OH^+ + OH^- \xrightarrow{k_2'} NH_3OH + H_2O \quad (2bis)$$

et on peut écrire:

$$\frac{d(NH_3OH)}{d(NH_3^+)} = \frac{k_2'(OH^-)}{k_2} \quad \text{ou encore la}$$

relation (III)

$$\frac{(NH_3OH)}{(NH_3^+)(OH^-)} = \frac{k_2'}{k_2} = K'$$

La constante K' correspond au rapport des deux vitesses n'est pas à véritablement parler une constante de dissociation puisque la réversibilité $NH_3OH \rightleftarrows (NH_3^+) + (OH^-)$ provient des deux voies de dissociation de NH_4OH^+ et ne correspond pas à un équilibre statique dans la solution.

A partir des concentrations en NH_3^+ et NH_2 ainsi définies, les réactions (4) et (8) ont lieu très rapidement mais sans les influencer. Comme ce sont des réactions de radicaux libres, on admet que les vitesses de l'équilibre véritable $NH_3^+ \rightleftarrows NH_2 + H^+$ sont trop lentes pour avoir le temps de modifier les vitesses de ces réactions (4) et (8) par déplacement d'équilibre. On aura alors sensiblement: $G(4)/G(8) = NH_2/(NH_3^+)$ et la valeur du pH au point d'inflexion correspondra à la fois à $G(4) = G(8)$ et à $(NH_2) = (NH_3^+)$

Quoi qu'il en soit nous accédons à une grandeur liée uniquement à la forme ionique ou neutre du radical NH_2 et nous écrirons la rélation(III) sous la forme:
$\log [(NH_2)/(NH_3^+)] = pH - pK'$, étant entendu que K' désigne le rapport des vitesses k_2'/k_2 et non une constante d'équilibre. On remarquera de façon plus générale qu'il

parait difficile d'appliquer la notion d'équilibre réversible à un système de radicaux libres éminemment réactifs. On a cependant gardé l'habitude en chimie sous rayonnement d'écrire ces équilibres (par exemple $HO_2 \rightleftarrows O_2^- + H^+$) et la notion de p$K$ relative aux constantes de dissociation est conservée par plusieurs auteurs.

La relation (III) peut s'écrire sous la forme:

$$(NH_2) = (NH_3^+) \exp [(pH - pK')/0{\cdot}434)] \quad \text{et différentiant}$$

$$\frac{d(NH_2)}{dt} = \frac{d(NH_3^+)}{dt} \exp\left(\frac{pH - pK'}{0{\cdot}434}\right) + \frac{(NH_3^+)}{0{\cdot}434} \cdot \frac{d(pH)}{dt} \exp\left(\frac{pH - pK'}{0{\cdot}434}\right)$$

(NH_3^+) est en faible concentration et la variation du pH en fonction du temps est lente, de sorte qu'on peut négliger le second terme et simplifier en:

$$\frac{d(NH_3^+)}{dt} = \frac{d(NH_2)}{dt} \exp\left(\frac{pK' - pH}{0{\cdot}434}\right)$$

et l'équation (II) peut s'écrire:

$$\frac{d(NH_2)}{D\,dt} + \frac{d(NH_2)}{D\,dt} \exp\left(\frac{pK' - pH}{0{\cdot}43}\right) = G_H$$

d'ou:

$$\frac{d(NH_2)}{D\,dt} = \frac{G_H}{1 + \exp\left[\dfrac{pK' - pH}{0{\cdot}43}\right]}$$

et d'après l'équation (I):

$$G(NH_3) = \frac{G_H}{1 + \exp [(pK - pH)/0{\cdot}43]}$$

En utilisant les constantes déterminées expérimentalement ci-dessus $G_H = 2{\cdot}7$ et $pK = 3{\cdot}65$ nous pouvons comparer les résultats obtenus expérimentalement et ceux obtenus en appliquant l'équation ci-dessus:

TABLEAU 2

pH_0	$G(NH_3)$ mesuré	$G(NH_3)$ calculé
6	2·7	2·70
4·4	2·3	2·30
0·5	0·00	0·002

L'équation:

$$G(NH_3) = \frac{G_H}{1 + \exp [(pK' - pH)/0{\cdot}43]}$$

peut s'écrire:

$$\frac{d(NH_3)}{dt} = \frac{DG_H}{1 + \exp [(pK' - pH)/0{\cdot}43]}$$

L'intégration de cette équation différentielle nous permet de trouver l'expression analytique des courbes obtenues expérimentalement à *condition de connaître la variation du* pH *en fonction du temps d'irradiation.*

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Le pH varie au cours de l'irradiation car en transformant l'hydroxyl-amine en azote nous libérons une quantité correspondante d'acide sulfurique.

D'autre part, nous transformons une partie de l'hydroxylamine de $pK = 6$ en ammoniaque de $pK = 9{\cdot}2$. Pour les solutions à pH initial égal à 6, il y a en plus de la soude qui neutralise une partie de l'acide libéré. Enfin, ces solutions sont tamponnées autour du pH 6, par l'hydroxylamine elle-même. Le pH variera donc de la valeur initiale 6, d'abord lentement, puis plus rapidement jusqu'à une valeur finale ou il ne variera que plus lentement.

Cette valeur finale du pH ne dépendra que de la concentration en acide sulfurique libre dont le pK de la deuxième acidité est deux. On peut calculer par exemple en se servant du graphique de FLOOD[12], que cette valeur finale sera voisine de trois. Expérimentalement, nous avons trouvé la variation donnée par la courbe en S de la Figure 1.

En première approximation, et nous verrons qu'elle est suffisante, nous pouvons assimiler cette courbe á une droite.

En effet, la Figure 1 montre que les rendements de formation de l'ammoniaque ne dépendent du pH de la solution que pour des pH compris entre 2·5 et 4·75.

D'autre part, les solutions irradiées à pH initial compris entre 4 et 7 voient leur pH diminuer au cours de l'irradiation jusqu'à une valeur limite voisine de 3·3. Il suffit donc que l'approximation analytique de la variation de pH en fonction du temps d'irradiation soit bonne pour les pH compris entre 3·3 et 4·75 ce qui est le cas pour la droite d'équation:

$$pH_0 - pH = \frac{3}{40} Dt \quad \text{pour} \quad 3{\cdot}3 \leq pH \leq 5.$$

Si nous portons cette expression dans l'équation différentielle ci-dessus nous obtenons:

$$\frac{d(NH_3)}{dt} = \frac{DG_H}{1 + e^{\beta+\gamma t}} \quad \text{avec} \quad \begin{cases} \beta = \dfrac{pK' - pH_0}{0{\cdot}43} \\ \gamma = \dfrac{3D}{40 \times 0{\cdot}43} \end{cases}$$

d'où:

$$(NH_3) = DG_H \int_0^t \frac{dt}{1 + e^{\beta+\gamma t}}$$

et en intégrant de zéro à t:

$$(NH_3) = DG_H \left[t + \frac{1}{\gamma} \log \frac{1 + e^{\beta}}{1 + e^{\beta+\gamma t}} \right]$$

Pour une solution de pH initial $pH_0 = 6$, $e^{\beta} = 1/225$ donc négligeable devant 1. Pour cette solution et pour un débit de dose absorbée de huit, exprimé en 10^{18} eV cm^{-1} hr^{-1}, la concentration d'ammoniaque en 10^{16} mol cm^{-1} aprés un temps d'irradiation t en heures s'exprime:

$$(NH_3) = 8G_H \left[t - \frac{1}{1{\cdot}39} \log (1 + e^{1{\cdot}39t - 5{\cdot}4}) \right]$$

comme nous avons trouvé $G_H = 2{\cdot}7$:

$$(NH_3)_{\text{en } 10^{16} \text{ mol/cm}^3} = 21{\cdot}6t_{\text{heures}} - 15{\cdot}5 \log_e (1 + e^{1{\cdot}39t - 5{\cdot}4})$$

[12] H. FLOOD, *Z. Electrochem.* **46**, 669 (1940).

On voit sur le Tableau 3, que cette fonction est en bon accord avec la courbe expérimentale jusqu'aux énergies absorbées égales á environ 40 10^{18} eV/cm^3.

A partir de ce point, la concentration en hydroxylamine n'est plus suffisante pour capter tous les radicaux, ce qui donne lieu à un abaissement supplémentaire des rendements.

TABLEAU 3

t	Dt	$(NH_3)_{calc.}$	$(NH_3)_{mes.}$
1	8	21·4	22
2	16	42·2	41
3	24	60·8	59
4	32	74·4	72
5	40	81·6	80

A pH initial égal à 4·4, la variation du pH en fonction du temps d'irradiation peut être représenté approximativement par la fonction:

$$pH_0 - pH = 0{\cdot}033\ Dt \quad \text{avec} \quad 3 < pH < 4{\cdot}4$$

$$\text{ou} \quad 0 < t < 5.$$

Dans les mêmes conditions que ci-dessus mais pour une solution de pH initial $pH_0 = 4{\cdot}4$, la quantité d'ammoniaque formée s'exprime en fonction du temps d'irradiation par l'équation:

$$(NH_3) = DG_H \left(t + \frac{1}{\gamma} \log \frac{1 + e^{\beta}}{1 + e^{\beta + \gamma t}} \right)$$

dans laquelle:

$$D = 8 \quad G_H = 2{\cdot}7 \quad \gamma = 0{\cdot}7 \quad \text{et} \quad \beta = -\frac{0{\cdot}75}{0{\cdot}4342} = -1{\cdot}73$$

d'où:

$$(NH_3) = 21{\cdot}6t + 5{\cdot}03 - 30{\cdot}8 \log_e (1 + e^{-1{\cdot}73 + 0{\cdot}7t})$$

TABLEAU 4(*a*)

t	$(NH_3)_{calc.}$	$(NH_3)_{exp.}$
1	15·8	16
2	31·6	31
3	42·2	42
4	49·2	50

Là encore on peut voir sur le tableau ci-contre que cette équation est en bon accord avec la courbe expérimentale (voir egalement Fig. 2).

A partir de $t = 4$, on peut admettre que le pH ne varie plus et qu'il reste égal à environ 3·4. Dans ce cas, l'équation de la courbe devient:

$$(NH_3) = (NH_3)_{t=4} + G(NH_3)_{pH=3{\cdot}4} D(t - t_4)$$

soit:

$$(NH_3)_{t>4} = 49{\cdot}2 + 7{\cdot}75(t - 4)$$

ce qui reste en bon accord avec l'expérience comme le montre le Tableau 4(*b*).

Nous pouvons faire un calcul analogue pour rendre compte de la destruction de

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l'hydroxylamine, dans la mesure ou la réaction (7) n'intervient pas, c'est-à-dire pour le pH initial de 4·4.

TABLEAU 4(*b*)

t	$(NH_3)_{calc.}$	$(NH_3)_{exp.}$
5	57	58
6	64·7	65
7	72·4	72
8	80	78

Nous avons en effet dans ce cas:

$$G(-NH_2OH) = G(OH) + G_H + G(NH_3) - 2G(NH_3^+)$$
$$= G_{H_2O_2} + G_{OH} + 2G_H - 3G(NH_3^+)$$

$$G(-NH_2OH) = G_{H_2O_2} + G_{OH} + 2G_H - \frac{3G_H}{1 + \exp[-(pK' - pH)/0{\cdot}43]}$$

En suivant le même mode de calcul que ci-dessus nous sommes conduits à l'équation:

$$-(NH_2OH) = (G_{H_2O_2} + G_{OH} - G_H)Dt + \frac{3G_H D}{\gamma} \log_e \left(\frac{1 + e^{-\beta}}{1 + e^{-\beta-\gamma t}}\right)$$

avec:

$$\beta = \frac{pK' - pH_0}{0{\cdot}43} = -1{\cdot}73$$

et:

$$\gamma = 0{\cdot}7$$

d'où:

$$-(NH_2OH) = 175 + 0{\cdot}96t - 92{\cdot}5 \log_e (1 + e^{1{\cdot}73 - 0{\cdot}7t}) \quad \text{pour} \quad 0 < t < 4$$

à partir de $t = 4$, le pH ne variant presque plus, nous avons comme pour l'ammoniaque

$$-(NH_2OH) = -(NH_2OH)_{t=4} + G(-NH_2OH)_{pH=3{\cdot}4} D(t - 4)$$

soit:

$$-(NH_2OH) = 151{\cdot}6 + 24(t - 4) \quad \text{pour} \quad t > 4.$$

Ces équations constituent une bonne représentation analytique des résultats expérimentaux comme le montre le tableau suivant:

TABLEAU 5

t	$-(NH_2OH)_{calc.}$	$-(NH_2OH)_{exp.}$	pH_0	$G(-NH_2OH)_{calc.}$	$G(-NH_2OH)_{exp.}$
1	52·0	51	6	8·1	8
2	96·0	94	4·4	7·0	7·1
3	129·0	126	3·4	3·0	—
4	151·6	151			
5	175.6	175			
6	199·6	196			

L'accord observé entre la courbe expérimentale exprimant la formation de l'ammoniaque en fonction de l'énergie absorbée dans la solution et l'expression analytique donnant cette formation en fonction du pH et de la dose absorbée justifie *l'hypothèse suivant laquelle le fait fondamental provoquant la baisse de rendement de formation de l'ammoniaque est uniquement le partage du radical* NH_2 *entre sa forme neutre et sa forme ionisée, la forme neutre donnant seule naissance a l'ammoniaque.*

D'autre part, l'équation analytique de la destruction de l'hydroxylamine montre que non seulement la forme ionisée ne réagit pas sur l'hydroxylamine mais que-celle-ci se reforme en partie égale á la quantité d'ions NH_3^+ formés.

Nous pensons que cet exemple illustre comment des informations peuvent être obtenues sur des composés instables par une étude cinétique des effets produits par les rayonnements ionisants, générateurs de radicaux libres au sein des solutions.

Decomposition spontanée de l'hydroxylamine

On a vu que l'hydroxylamine en solutions aqueuses est relativement instable surtout en milieu alcalin. L'autodécomposition est déja appréciable à pH 8 et conduit exclusivement à l'ammoniaque et à l'azote selon l'équation globale déjà indiquée:

$$3NH_2OH \rightarrow NH_3 + N_2 + 3H_2O$$

Un mécanisme de cette décomposition, dont on sait qu'elle est initiée par divers catalyseurs, peut être proposé à la lumière des résultats précédents et de leur interprétation. On peut envisager l'attaque d'une molécule d'hydroxylamine par une autre molécule du même composé, de façon à rompre la liaison NH_2—OH et libérer un radical NH_2

$$NH_2 - OH + NH_2OH \rightarrow NH_2 + N\,HOH + H_2O \qquad (10)$$

Cependant cette réaction (10) risque d'être endothermique et d'avoir besoin d'être initiée par un catalyseur. On connait l'importance des ions de cuivre ou des ions ferreux; On peut supposer par exemple que (10) se passe en 2 étapes:

$$NH_2OH + Fe^{2+} \rightarrow NH_2 + FeOH^{2+}$$

$$NH_2OH + FeOH^{2+} \rightarrow NHOH + Fe^{2+} + H_2O$$

Quel que soit le mode d'attaque, on est conduit comme par le rayonnement à la formation de NHOH et de NH_2 et aux réactions (3) et (4). Ainsi par (10) et (4) trois molécules d'hydroxylamine produisent une molécule d'ammoniaque et par la dimérisation (3) une molécule d'azote. Lorsque le pH est plus faible, l'ion hydroxylamonium NH_3OH^+ et l'ion NH_3^+ ne peuvent plus réagir selon (4) en raison de la répulsion électrostatique. Même si la réaction (10) a pû être catalysée, la réaction inverse (8) que nous avons déjà examinée reforme l'hydroxylamine. On expliquerait ainsi la stabilitéen milieu acide.

APPENDICE

Méthodes analytiques

Les solutions préalablement soigneusement dégazées étaient irradiées selon les méthodes du Laboratoire déjá décrites.[1] La microanalyse des gaz formés (N_2, N_2O, NO, H_2 et éventuellement O_2) a été conduite soit par chromatographie par adsorption,[13] soit avec un appareil utilisant un alphamètre.[14] On indiquera ici seulement les méthodes utilisées pour mesurer l'hydroxylamine

[13] M. LEFORT et X. TARRAGO, *J. Chromatography* **2**, 218 (1959).
[14] M. LEFORT, *Bull. Soc. Chim.* 253 (1960).

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l'ammoniaque. On a vérifié par ailleurs, par des méthodes de détection très sensibles l'absence de nitrites, de nitrates et d'hydrazine dans les solutions irradiées en absence d'oxygène.

(a) *Dosage de l'hydroxylamine**

On oxyde l'hydroxylamine par l'iode en milieu acétique et en présence d'acide sulfanilique. On obtient ainsi le diazoïque de l'acide sulfanilique que l'on copule avec le chlorhydrate d'α-naphtyl-éthylène-diamine suivant la méthode de GRIESS[15]

Les réactifs employés sont les suivants:

Acide sulfanilique 2·5 g dans 200 ml d'eau. On dissout à chaud, puis on laisse refroidir et on ajoute 50 ml d'acide acétique pur.

Chlorhydrate d'α-naphtyl-éthylène-diamine à 0·1 per cent dans de l'eau légèrement chlorhydrique.

Iode: solution acétique d'iode à 0·65 g pour 100 ml d'acide acétique.

Hyposulfite de soude à 2 per cent.

Mode opératoire. Dans une fiole jaugée de 10 ml, on introduit l'échantillon à doser contenant environ 30×10^{15} molecules. On ajoute 1 ml de la solution d'acide sulfanilique et on thermostate à 25 C. Lorsque l'équilibre thermique est réalisé, on ajoute 0·2 ml de la solution acétique d'iode et on laisse l'oxydation de l'hydroxylamine et la diazotation de l'acide sulfanilique se poursuivre pendant exactement 5 min. Au bout de ce temps, on détruit l'excès d'iode par l'hyposulfite de soude, ceci à la goutte près. On laisse ensuite pendant 3–4 min et on ajoute 1 ml de copulant (α-naphtyl-éthylène-diamine-chlorhydrate). On laisse 3–5 min et on complète à 10 ml avec de l'eau.

On obtient une coloration rouge, stable pendant plus d'une demi-heure, que l'on dose au spectrophotomètre JOBIN & YVON à 540 mμ. On dose ainsi la somme hydroxylamine plus nitrites. Si c'est la concentration globale de ces 2 corps en 10^{15} molécules par cm^3 et d, la densité optique de la solution placée dans une cuve de 1 cm d'épaisseur par rapport à un témoin contenant les réactifs seuls et placé dans les mêmes conditions, on a dans la solution finale $c = 1{\cdot}33\,d$. Dans le présent travail, la prise d'essai correspond de 0·1–0·01 ml de la solution irradiée. La méthode est très sensible et les résultats sont reproductibles si les conditions de la diazotation sont elles-mêmes exactement reproduites. La coloration rouge obtenue suit la loi de Lambert-Beer au moins pour les densités optiques comprises entre 0 et 0·8. Les conditions expérimentales du dosage que nous avons adoptées sont celles qui donnent les mêmes résultats pour des solutions étalons de chlorhydrate d'hydroxylamine R.P., de sulfate d'hydroxylamine pur et de nitrite de sodium R.P. Cependant, les conditions d'oxydation de l'hydroxylamine et de diazotation de l'acide sulfanilique en présence d'iode jouent un grand rôle dans le résultat obtenu finalement. Pour être sur des dosages des solutions inconnues, nous avons dosé en même temps une solution témoin de concentration connue.

Pour doser les nitrites, nous avons utilisé la même méthode que pour le dosage de l'hydroxylamine, en supprimant la réaction d'oxydation de celle-ci, c'est-à-dire sans ajouter l'iode.

(b) *Dosage de l'ammoniaque*

La méthode utilisée est celle mise au point par LUBOCHINSKY et ZALTA[16]. Nous l'avons toutefois un peu modifiée pour permettre le dosage de très faibles quantités d'ammoniaque en présence de grandes quantités d'hydroxylamine.

Par cette méthode, on forme l'indophénol chloré, bleu, à partir du phénol en présence d'hypochlorite et de nitroprussiate de soude à pH = 12. On dose l'indophénol par spectrophotométrie à 630 mμ.

La coloration bleue obtenue se stabilise au bout d'une demi-heure et reste stable pendant plusieurs heures. La méthode a été controlée, d'une part avec des solutions connues de sulfate d'ammonium, d'autre part avec des solutions connues contenant à la fois du sulfate d'ammonium et d'hydroxylamine. L'hydroxylamine interfère dans le dosage lorsque sa concentration est dix fois supérieure à celle de l'ammoniaque. Dans ce cas, il faut retirer du résultat obtenu, $0{\cdot}7 \times 10^{16}$ molecules/ml pour 10×10^{16} molécules/cm^3 d'hydroxylamine présente. Pour les solutions 5×10^{-3} M d'hydroxylamine irradiées avec des doses faibles, nous avons dosé les solutions irradiées en même temps que des solutions de

* Mr. LEBAIL a participé à la mise au point de cette technique et nous le remercions ici très sincèrement de son aide.

(15) F. D. SNELL et C. T. SNELL, *Calorimétrie Méthodes of Analysis*. II. Van Nostrand, New York (1949).
(16) B. LUBOCHINSKY et J. P. ZALTA, *Bull. Soc. Chim. Biol.* **36**, 1363 (1954).

composition très voisine et connue, préparées à l'avance. Par comparaison des résultats obtenus, nous en avons déduit la concentration réelle en ammoniaque des solution irradiées. Pour doser de très faibles quantités d'ammoniaque, de l'ordre de 3 ou 4 $\times$ 10^{16} molécules par cm^3, en présence de 300 $\times$ 10^{16} molécules/ml d'hydroxylamine, nous avons obtenu de très bons résultats en détruisant avant le dosage, l'hydroxylamine présente par du permanganate de potassium en solution acide.

Si C est la concentration en ammoniaque dans la solution finale, en 10^{16} molécule/cm^3 et d la densité optique mesurée à 630 mμ par rapport à un témoin ne contenant que les réactifs on a $C = 3{\cdot}1\,d$ pour une épaisseur de 1 cm.

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THE USE OF THE RELAXATION METHOD IN THE COMPUTATION OF SUCCESSIVE COMPLEXITY CONSTANTS

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RELAXATION methods have been designed primarily to provide numerical solutions to physical problems which can be expressed mathematically in a linear form.[1,2] This method is applicable to any problem which is reducible to the solution of a system of non-homogeneous, linear, simultaneous, algebraic equations in a finite number of unknown variables. The determination of successive stability constants for complexes by the common experimental procedures ultimately yields such a set of equations. We have therefore examined the use of this method in computing stability constants using data obtained by

(a) LEDEN's method,[3]
(b) BJERRUM's method,[4]
(c) ERIKSSON's polarographic method,[5,6] and
(d) the polarographic method of DEFORD and HUME[7,8].

A general procedure is used in setting up the relaxation method in each case. The sets of equations are reduced to the desired linear form with all the terms on one side and zero on the other. New quantities, called the residuals, are introduced in place of the zeros. For any value assigned to the unknowns, the residuals will have certain values. For those values which are solutions the residuals will be zero. The equations are solved by a process which reduces these residuals to arbitrarily small values. For an *exact* solution the residuals must be zero, but approximate solutions can be obtained by reducing these residuals to small fractions of their original values. The relaxation method is a procedure involving various operations designed to reduce these residuals.

The first step is the construction of the unit operations table (see below) which shows how a unit change in the value of each variable affects the value of each residual of a set of equations. The second step is the construction of the relaxation table. The table has a vertical column for each of the residuals as well as one in which the sequence of operations is recorded. These operations may involve

(1) the unit operations applied one at a time generally in such a manner as to reduce the largest residual,
(2) group relaxation in which all the values of the variable are changed at once
(3) the use of multiplying factors, and
(4) overrelaxation or underrelaxation.[1,2]

[1] F. S. SHAW, *An Introduction to Relaxation Methods* pp. 1–25, Dover Publications, New York (1953).
[2] D. N. DE G. ALLEN, *Relaxation Methods* pp. 1–23, McGraw-Hill, New York.
[3] I. LEDEN, *Z. Physik. Chem.* **188**, 160 (1941).
[4] J. BJERRUM, *Metal Amine Formation in Aqueous Solution* p. 27 ff. P. Haase, Copenhagen (1941 and 1957).
[5] L. ERIKSSON and A. RINGBOM, *Acta Chem. Scand.* **7**, 1105 (1953).
[6] L. ERIKSSON, *Acta Chem. Scand.* **7**, 1146 (1953).
[7] D. D. DEFORD and D. N. HUME, *J. Amer. Chem. Soc.* **73**, 5321 (1951).
[8] D. D. DEFORD, D. N. HUME and G. C. B. CAVE, *J. Amer. Chem. Soc.* **73**, 5323 (1951).

The use of this method is best illustrated by its application to specific cases. Further information on specific details may be obtained from the texts of SHAW[1] and ALLEN.[2]

USE WITH LEDEN'S PROCEDURE[3]

The method of LEDEN is commonly used to study weak complexes in a system where the metal ion concentration can be directly measured using a reversible electrode. Thus for a system of complexes involving cadmium ion and some monodentate anionic species A^-, the complexation equilibria are:

$$Cd^{2+} + A^- \rightarrow CdA^+ \tag{1}$$

$$Cd^{2+} + 2A^- \rightarrow CdA_2 \tag{2}$$

$$Cd^{2+} + iA^- \rightarrow CdA_i \tag{3}$$

and the overall stability constants are:

$$\beta_i = \frac{[CdA_i]}{[Cd^{2+}][A^-]^i} \tag{4}$$

If we let

$$x = [Cd^{2+}] + \Sigma\,[CdA_i] \tag{5}$$

$$y = [A^-] + \Sigma\, i[CdA_i] \tag{6}$$

then

$$\frac{x - [Cd^{2+}]}{[Cd^{2+}][A^-]} = \Sigma\,\beta_i[A^-]^{(i-1)} = \beta_1 + \beta_2[A^-] + \beta_3[A^-]^2 + \beta_4[A^-]^3 \ldots = F(A) \tag{7}$$

Designating N as the average number of ligands per *complex ion*:

$$N = \frac{\Sigma\, i[CdA_i]}{\Sigma\,[CdA_i]} = \frac{\Sigma\, i\beta_i[A^-]^{(i-1)}}{\Sigma\,\beta_i[A^-]^{(i-1)}} \tag{8}$$

The relaxation method uses the series of equations for $F(A)$; one equation is required for each equilibrium constant. Because of the inherent nature of this method, the data obtained must be reduced by a series of successive approximations. The steps followed are listed below:

(1) Preliminary values of $F(A)$ are computed for the various points on the titration curve using the equations connecting the potentials measured at adjacent points with N:

$$E_1 - E_2 = \frac{RT}{2F} N(\ln [A^-]_1 - \ln [A^-]_2) \approx \frac{RT}{2F} (\ln y_1 - \ln y_2) \tag{9}$$

The $[A^-]$ is obtained from:

$$[A^-] = y - N(x - [Cd^{2+}]) \tag{10}$$

and $F(A)$ is computed from the defining equation.

(2) A relaxation table is set up and the relaxation process is carried to a stage where the residuals have satisfactorily small values.

(3) The β_i's determined in this way are used to determine more accurate values of N from its defining equation and then more accurate values of $[A^-]$. From these more accurate values a new set of $F(A)$ values are computed.

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(4) The relaxation method is used with these new $F(A)$ values to get better β_i's and these steps are repeated until the β_i's do not change.

The data obtained by LEDEN on the Cd^{2+}–Br^- system can be used with this method to obtain as many equations as desired of the form

$$F(K) = \beta_1 + \beta_2[A^-] + \beta_3[A^-]^2 + \beta_4[A^-]^3 - F(A) \tag{11}$$

where $F(K)$ is the residual. For typical data from LEDEN's paper, seven such equations are:

$$F(T) = \beta_1 + \beta_2(8{\cdot}700 \times 10^{-3}) + \beta_3(7{\cdot}569 \times 10^{-5}) + \beta_4(6{\cdot}585 \times 10^{-7}) - 59{\cdot}1 \tag{12}$$

$$F(U) = \beta_1 + \beta_2(2{\cdot}670 \times 10^{-2}) + \beta_3(7{\cdot}129 \times 10^{-4}) + \beta_4(1{\cdot}903 \times 10^{-5}) - 63{\cdot}9 \tag{13}$$

$$F(V) = \beta_1 + \beta_2(4{\cdot}440 \times 10^{-2}) + \beta_3(1{\cdot}971 \times 10^{-3}) + \beta_4(8{\cdot}751 \times 10^{-5}) - 72{\cdot}6 \tag{14}$$

$$F(W) = \beta_1 + \beta_2(6{\cdot}570 \times 10^{-2}) + \beta_3(4{\cdot}316 \times 10^{-3}) + \beta_4(2{\cdot}836 \times 10^{-4}) - 85{\cdot}7 \tag{15}$$

$$F(X) = \beta_1 + \beta_2(8{\cdot}610 \times 10^{-2}) + \beta_3(7{\cdot}413 \times 10^{-3}) + \beta_4(6{\cdot}383 \times 10^{-4}) - 98{\cdot}7 \tag{16}$$

$$F(Y) = \beta_1 + \beta_2(1{\cdot}600 \times 10^{-1}) + \beta_3(2{\cdot}560 \times 10^{-2}) + \beta_4(4{\cdot}096 \times 10^{-3}) - 170 \tag{17}$$

$$F(Z) = \beta_1 + \beta_2(2{\cdot}230 \times 10^{-1}) + \beta_3(4{\cdot}973 \times 10^{-2}) + \beta_4(1{\cdot}109 \times 10^{-2}) - 270 \tag{18}$$

One assumption of this, as well as other algebraic methods, is that the numbers used are exact. The construction of the unit operations table for this set of equations results in:

	$F(T)$	$F(U)$	$F(V)$	$F(W)$	$F(X)$	$F(Y)$	$F(Z)$
$\Delta\beta_1 = 1$	1·000	1·000	1·000	1·000	1·000	1·000	1·000
$\Delta\beta_2 = 1$	$8{\cdot}700 \times 10^{-3}$	$2{\cdot}670 \times 10^{-2}$	$4{\cdot}440 \times 10^{-2}$	$6{\cdot}570 \times 10^{-2}$	$8{\cdot}610 \times 10^{-2}$	$1{\cdot}600 \times 10^{-1}$	$2{\cdot}230 \times 10^{-1}$
$\Delta\beta_3 = 1$	$7{\cdot}569 \times 10^{-5}$	$7{\cdot}129 \times 10^{-4}$	$1{\cdot}971 \times 10^{-3}$	$4{\cdot}316 \times 10^{-3}$	$7{\cdot}413 \times 10^{-3}$	$2{\cdot}560 \times 10^{-2}$	$4{\cdot}973 \times 10^{-2}$
$\Delta\beta_4 = 1$	$6{\cdot}585 \times 10^{-7}$	$1{\cdot}903 \times 10^{-5}$	$8{\cdot}751 \times 10^{-5}$	$2{\cdot}836 \times 10^{-4}$	$6{\cdot}383 \times 10^{-4}$	$4{\cdot}096 \times 10^{-3}$	$1{\cdot}109 \times 10^{-2}$

The relaxation table is then constructed; one way is shown below.

	$F(T)$	$F(U)$	$F(V)$	$F(W)$	$F(X)$	$F(Y)$	$F(Z)$
$\Delta\beta_i$'s = 0	−59·100	−63·900	−72·600	−85·700	−98·700	−170·00	−270·000
$\Delta\beta_1 = 5{\cdot}9 \times 10^1$	−0·100	−4·900	−13·600	−26·700	−39·700	−111·00	−211·000
$\Delta\beta_2 = 2 \times 10^2$	+1·640	+0·440	−4·720	−13·560	−22·480	−79·00	−166·400
$\Delta\beta_3 = 2 \times 10^3$	+1·791	+1·860	−0·780	−4·928	−7·654	−27·80	−66·942
$\Delta\beta_4 = 1 \times 10^4$	+1·798	+2·05	+0·095	−2·092	−1·271	+13·16	+43·598
$\Delta\beta_2 = 2 \times 10^1$	+1·972	+2·584	+0·983	−0·778	+0·451	+16·36	+48·418
$\Delta\beta_1 = -2$	−0·028	+0·584	−1·017	−2·778	−1·549	+14·36	+46·418
$\Delta\beta_4 = -4 \times 10^3$	−0·030	+0·508	−1·367	−3·912	−4·102	−2·024	+2·058

After the residuals have been reduced to suitably small values, the values of the constants are obtained by merely summing up the changes which have been made in each of the variables. In the present case this results in: $\beta_1 = \Sigma\ \Delta\beta_1 = 57$; $\beta_2 = \Sigma\ \Delta\beta_2 = 220$; $\beta_3 = \Sigma\ \Delta\beta_3 = 2 \times 10^3$; $\beta_4 = \Sigma\ \Delta\beta_4 = 6 \times 10^3$. These values are to be compared with the values obtained by Leden using graphical methods: $\beta_1 = 57$; $\beta_2 = 220$; $\beta_3 = 2{\cdot}1 \times 10^3$; $\beta_4 = 5 \times 10^3$.

USE WITH BJERRUM'S PROCEDURE[4]

The basic equation for this procedure is the one relating $\bar{n}$, the average number of ligands bound per metal ion in solution, to the various cumulative stability constants K_n, and the concentration of free co-ordinating species [A]. This is

$$\bar{n} = \frac{\sum_{n=1}^{n=N} nK_n[\mathrm{A}]^n}{1 + \sum_{n=1}^{n=N} K_n[\mathrm{A}]^n} \tag{19}$$

In order to put this into the desired form it is written as

$$\sum_{n=1}^{n=N} (n - \bar{n})K_n[\mathrm{A}]^n - \bar{n} = F(X) \tag{20}$$

Now [A] is determined experimentally and $\bar{n}$ is obtained from the relation:

$$\bar{n} = \frac{C_\mathrm{A} - [\mathrm{A}]}{C_\mathrm{M}} \tag{21}$$

where C_A and C_M are the total concentrations of A and M in solution respectively, and [A] is the concentration of free co-ordinating species. The data required for the determination of the K_n's are the typical $\bar{n}$, [A] data. The data on the Zn^{2+}–NH_3 system in 2 M NH_4NO_3 are available in BJERRUM's thesis; typical values are:

$[NH_3] = [A] =$	$2{\cdot}00 \times 10^{-3}$	$2{\cdot}81 \times 10^{-3}$	$3{\cdot}61 \times 10^{-3}$	$4{\cdot}66 \times 10^{-3}$
$\bar{n} =$	0·889	1·342	1·789	2·244

These data lead to the four equations:

$$F(W) = 2{\cdot}220 \times 10^{-4}\mathrm{K}_1 + 4{\cdot}444 \times 10^{-6}\mathrm{K}_2 + 1{\cdot}689 \times 10^{-8}\mathrm{K}_3 + 4{\cdot}976 \times 10^{-11}\mathrm{K}_4 - 0{\cdot}889 \tag{22}$$

$$F(X) = -9{\cdot}610 \times 10^{-4}\mathrm{K}_1 + 5{\cdot}196 \times 10^{-6}\mathrm{K}_2 + 3{\cdot}679 + 10^{-8}\mathrm{K}_3 + 1{\cdot}657 \times 10^{-10}\mathrm{K}_4 - 1{\cdot}342 \tag{23}$$

$$F(Y) = -2{\cdot}848 \times 10^{-3}\mathrm{K}_1 + 2{\cdot}750 \times 10^{-6}\mathrm{K}_2 + 5{\cdot}697 \times 10^{-8}\mathrm{K}_3 + 3{\cdot}755 \times 10^{-10}\mathrm{K}_4 - 1{\cdot}789 \tag{24}$$

$$F(Z) = -5{\cdot}797 \times 10^{-3}\mathrm{K}_1 - 5{\cdot}299 \times 10^{-6}\mathrm{K}_2 + 7{\cdot}650 \times 10^{-8}\mathrm{K}_3 + 8{\cdot}281 \times 10^{-10}\mathrm{K}_4 - 2{\cdot}244 \tag{25}$$

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For this set of equations, the unit operations table is:

	$\Delta F(W)$	$\Delta F(X)$	$\Delta F(Y)$	$\Delta F(Z)$
$\Delta K_1 = 1$	$2{\cdot}220 \times 10^{-4}$	$-9{\cdot}610 \times 10^{-4}$	$-2{\cdot}848 \times 10^{-3}$	$-5{\cdot}797 \times 10^{-3}$
$\Delta K_2 = 1$	$4{\cdot}440 \times 10^{-6}$	$5{\cdot}196 \times 10^{-6}$	$2{\cdot}749 \times 10^{-6}$	$-5{\cdot}299 \times 10^{-6}$
$\Delta K_3 = 1$	$1{\cdot}689 \times 10^{-8}$	$3{\cdot}679 \times 10^{-8}$	$5{\cdot}697 \times 10^{-8}$	$7{\cdot}650 \times 10^{-8}$
$\Delta K_4 = 1$	$4{\cdot}976 \times 10^{-11}$	$1{\cdot}657 \times 10^{-10}$	$3{\cdot}755 \times 10^{-10}$	$8{\cdot}281 \times 10^{-10}$

and the relaxation table is:

	$F(W)$	$F(X)$	$F(Y)$	$F(Z)$
ΔK_i's $= 0$	$-0{\cdot}889$	$-1{\cdot}342$	$-1{\cdot}789$	$-2{\cdot}244$
$\Delta K_4 = 3 \times 10^9$	$-0{\cdot}740$	$-0{\cdot}845$	$-0{\cdot}662$	$+0{\cdot}240$
$\Delta K_3 = 1 \times 10^7$	$-0{\cdot}571$	$-0{\cdot}477$	$-0{\cdot}092$	$+1{\cdot}005$
$\Delta K_2 = 8 \times 10^4$	$-0{\cdot}215$	$-0{\cdot}061$	$+0{\cdot}128$	$+0{\cdot}581$
$\Delta K_1 = 4 \times 10^2$	$-0{\cdot}126$	$-0{\cdot}445$	$-1{\cdot}011$	$-1{\cdot}738$
$\Delta K_2 = 1 \times 10^7$	$+0{\cdot}043$	$-0{\cdot}077$	$-0{\cdot}441$	$-0{\cdot}973$
$\Delta K_4 = -1{\cdot}5 \times 10^9$	$+0{\cdot}013$	$+0{\cdot}066$	$-0{\cdot}014$	$-0{\cdot}104$

The cumulative constants are obtained by summing up the changes in each of the variables and are found to be $K_1 = 2{\cdot}5 \times 10^2$, $K_2 = 8 \times 10^4$, $K_3 = 2 \times 10^7$, and $K_4 = 3 \times 10^9$. A comparison of the logarithms of the cumulative constants obtained by the relaxation method with those of BJERRUM's values is given below.

	$K_1 = k_1$	$K_2 = k_1k_2$	$K_3 = k_1k_2k_3$	$K_4 = k_1k_2k_3k_4$
BJERRUM's thesis	2·37	4·81	7·31	9·46
Relaxation method	2·40	4·90	7·30	9·48

The same kind of equations are obtained with BJERRUM's method of corresponding solutions[9] and the relaxation method in this case is carried out in a strictly analogous fashion.

ERIKSSON'S POLAROGRAPHIC METHOD[5,6]

This procedure was devised for the polarographic determination of consecutive complexity constants. If suitable indicator ions are present, the method may be used even though the central metal ion is not reduced. The complexity constants are obtained by the solution of linear equations of the same type as are encountered in LEDEN's method:

$$F_1 = \beta_1 + \beta_2 A_0 + \beta_3 A_0^2 + \beta_4 A_0^3 \tag{26}$$

where the A_0 values, the concentration of free ligand, are obtained in the following manner:

(1) The average ligand number of the system, $\bar{n}$, is expressed as

$$\bar{n} = \frac{\text{total number of bound ligands}}{\text{total number of metal atoms}} \tag{27}$$

where $\bar{n}$ can be calculated from Bodlander's equation:

$$\bar{n} = \frac{-dE}{d \ln A} \cdot \frac{mF}{RT} \tag{28}$$

[9] J. BJERRUM, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **21**, No. 4 (1944).

Here, m equals the valency of the metal ion, A represents the concentration of free ligand, and E is the potential.

For a bivalent metal ion system at 25°C, equation (28) becomes

$$\bar{n}_0 = \frac{-d\,\Delta E}{d \log A_0} \cdot \frac{1}{29{\cdot}58} \tag{29}$$

where the subscript 0 refers to concentrations at the electrode surface.

(2) Values of ΔE, the difference between the potential of a metal perchlorate solution with ligand present and without any ligand present at a specified current, can be obtained from polarograms taken at various ligand concentrations. The potentials are expressed as a fraction of the diffusion current, i_d, *e.g.* i/i_d.

(3) Since A_0 is not known, the total concentration of A in the system, C_A, is used as a first approximation to obtain $\bar{n}_0$ values. For a system such as Cd^{2+}–Br^- or Cd^{2+}–Cl^-, the differences between C_A and A_0 are small. The approximate $\bar{n}_0$ values obtained from (29) are used to compute new values of A_0 from the equation

$$A_0 = C_A - \bar{n}_0 \cdot \frac{i_d - i}{i_d} C_M \tag{30}$$

With these new A_0 values, new values of $\bar{n}_0$ are computed using the Bodlander equation.

(4) The concentration of the metal ion at the electrode surface, M_0, is calculated from the equation

$$\Delta E = -29{\cdot}58 \log \frac{C_{0M}}{M_0} \tag{31}$$

where C_{0M} represents the total metal ion concentration at the drop surface, $\frac{i_d - i}{i_d} C_M$

(5) To calculate the β's, functions F_n are introduced and defined as:

$$F_n = \frac{F_1}{A_0^{(n-1)}} = \frac{C_{0M} - M_0}{M_0 \cdot A_0^n} = \frac{\frac{C_{0M}}{M_0} - 1}{A_0^n}$$

Values of F_n corresponding to various values of A_0 can then be determined. ERIKSSON obtained the following data on the Cd^{2+}–Br^- system in a medium whose ionic strength was three.

$[Br^-] \times 10^3$	274·8	499·5	691·9	999·0
F_1	370·0	1328·0	3005·0	7160·0

The following equations for the relaxation process can be obtained from this data.

$$F(W) = \beta_1 + 0{\cdot}2748\beta_2 + 0{\cdot}07552\beta_3 + 0{\cdot}02075\beta_4 - 370 \tag{33}$$

$$F(X) = \beta_1 + 0{\cdot}4995\beta_2 + 0{\cdot}2495\beta_3 + 0{\cdot}1246\beta_4 - 1328 \tag{34}$$

$$F(Y) = \beta_1 + 0{\cdot}6919\beta_2 + 0{\cdot}4787\beta_3 + 0{\cdot}3312\beta_4 - 3005 \tag{35}$$

$$F(Z) = \beta_1 + 0{\cdot}9990\beta_2 + 0{\cdot}9980\beta_3 + 0{\cdot}9970\beta_4 - 7160 \tag{36}$$

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The table of unit operation is:

	$F(W)$	$F(X)$	$F(Y)$	$F(Z)$
$\Delta\beta_1 = 1$	1·00000	1·00000	1·00000	1·00000
$\Delta\beta_2 = 1$	0·27480	0·49950	0·69190	0·99900
$\Delta\beta_3 = 1$	0·07552	0·24950	0·47870	0·99800
$\Delta\beta_4 = 1$	0·02075	0·12460	0·33120	0·99700
$\Delta\beta_1 = \Delta\beta_2 = \Delta\beta_3 = \Delta\beta_4 = 1$	1·37100	1·87400	2·50200	3·99400

The relaxation table constructed for these equations is:

$\Delta\beta_i$'s $= 0$	−370·00	−1328·00	−3005·00	−7160·00
$\Delta\beta_i$'s $= 2 \times 10^2$	−95·80	−953·20	−2504·60	−6361·20
$\Delta\beta_4 = 6 \times 10^3$	+28·70	−205·60	−517·40	−379·20
$\Delta\beta_3 = 1 \times 10^3$	+104·22	+43·90	−38·70	+618·80
$\Delta\beta_2 = 1 \times 10^3$	+131·70	+93·85	+30·49	+718·70
$\Delta\beta_i$'s $= -1 \times 10^2$	−5·40	−93·55	−219·71	+319·30
$\Delta\beta_4 = -4 \times 10^2$	−13·70	−143·39	−352·19	−79·50
$\Delta\beta_3 = 7 \times 10^2$	+39·16	+31·26	−17·10	+619·10
$\Delta\beta_1 = -4 \times 10^1$	−0·84	−8·74	−57·10	+579·10
$\Delta\beta_4 = -3 \times 10^2$	−7·07	−46·12	−156·46	+280·00
$\Delta\beta_2 = 1 \times 10^2$	+0·48	−21·17	−108·59	+379·80

On summing up the operations one obtains: $\beta_1 = \Sigma\,\Delta\beta_1 = 60$, $\beta_2 = \Sigma\,\Delta\beta_2 = 200$ $\beta_3 = \Sigma\,\Delta\beta_3 = 1900$, $\beta_4 = \Sigma\,\Delta\beta_4 = 5400$. The residuals have been reduced to approximately $\frac{1}{20}$ of their original values. ERIKSSON's constants are $\beta_1 = 58 \pm 2$, $\beta_2 = 275 \pm 25$, $\beta_3 = 1600 \pm 200$, and $\beta_4 = 5400 \pm 400$.

THE POLAROGRAPHIC METHOD OF DEFORD AND HUME[7,8]

This method is useful in studying complex ions which are reversibly reduced at the dropping mercury electrode. By an analysis of the shift of half-wave potential with ligand concentration, the successive complex ions which are formed can be identified and this then permits the evaluation of the formation constants.

If the electrode reactions are reversible, the potential of the dropping mercury electrode is given by:

$$E_{\text{d.e.}} = E_a^\circ - \frac{RT}{nF} \ln \frac{C_a^\circ f_a}{C_M^\circ f_M} \tag{37}$$

where C_a° is the concentration of the amalgam at the electrode surface, C_M° is the concentration of the simple metal ions at the electrode surface, and the f's are the corresponding activity coefficients. Since the amalgam formed at the electrode surface is very dilute, f_a is considered to be unity.

If the formation of the complex ion is rapid and reversible, a formation constant may be written for each individual complex:

$$C_{MXJ} f_{MXJ} = K_j C_M f_M (C_X)^j (f_X)^j \tag{38}$$

Here, C_{MXJ} is the concentration of the complex $MX_j^{+(n-jd)}$ in the body of the solution, K_j is the formation constant of the complex, C_M and C_X are the concentrations of the

simple metal ion and ligand species, respectively, in the body of the solution. The f's are the corresponding activity coefficients.

By addition of equations of the type (38) one may obtain:

$$C_M^\circ f_M = \frac{\sum_j C^\circ_{MX_j}}{\sum_j \left\{\frac{K_j (C_X)^j (f_X)^j}{f_{MX_j}}\right\}} \tag{39}$$

and by combining equations (37) and (39) one obtains:

$$E_{d.e.} = E_a^\circ - \frac{RT}{nF} \ln C_a^\circ \frac{\sum_j \left\{\frac{K_j (C_X)^j (f_X)^j}{f_{MX_j}}\right\}}{\sum_j C^\circ_{MX_j}} \tag{40}$$

By assuming the presence of excess supporting electrolyte to eliminate the migration current, it is possible to show that the half-wave potential of the reducible ion in the presence of the complex forming substance can be given by

$$(E_{\frac{1}{2}})_c = E_a^\circ - \frac{RT}{nF} \ln \frac{I_c}{I_M} \sum_j \left\{\frac{k_j (C_X)^j f_X{}^j}{f_{MX_j}}\right\} \tag{41}$$

where I_c represents the measurable diffusion current constant and I_M the diffusion current constant of the metal atoms of mercury.

In an analogous manner the half-wave potential of the simple ion can be shown to be

$$(E_{\frac{1}{2}})_s = E_a^\circ - \frac{RT}{nF} \ln \frac{I_s}{f_s I_M} \tag{42}$$

When the activity coefficient of the ion is unity the half-wave potential is given by

$$(E_{\frac{1}{2}}^\circ)_s = (E_{\frac{1}{2}})_s - \frac{RT}{nF} \ln f_s = E_a^\circ - \frac{RT}{nF} \ln (I_s/I_M) \tag{43}$$

Combination of equations (41) and (43) gives, on rearrangement

$$F_0(X) = \sum_j \left\{\frac{K_j C_X{}^j f_X{}^j}{f_{MX_j}}\right\} = \text{antilog} \left\{0{\cdot}435 \frac{nF}{RT} [(E_{\frac{1}{2}})_s - (E_{\frac{1}{2}})_c] + \log (I_s/I_c)\right\} \tag{44}$$

$F_0(X)$ is the experimentally measured quantity, K_j is the formation constant of the complex $MX_j^{+(n-jb)}$, C_X is the concentration of the free ligand species. If the activity coefficients are assumed to be unity, equation (44) reduces to:

$$F_0(X) = \sum_{j=0}^{j=X} K_j C_X{}^j \tag{45}$$

The function $F_1(X)$ is introduced and defined by the equation:

$$F_1(X) = [F_0(X) - K_0]/C_X \tag{46}$$

and $F_2(X)$ defined by:

$$F_2(X) = [F_1(X) - K_1]/C_X \quad \text{etc.} \tag{47}$$

in a manner similar to that used by LEDEN. The relaxation method requires only the

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$F_0(X)$ function to obtain equations suitable for solution. Thus for a system such as the Cd^{2+}–SCN^- system studied by HUME, *et al.*[9], sets of equations of the form

$$F_0(X) = \sum_{j=0}^{j=4} K_j[CNS^-]^j \tag{48}$$

are used. Typical $F_0(CNS^-)$ values reported by these workers are:

KCNS (M)	0·4	0·5	0·7	1·0	1·5	2·0
$F_0(CNS^-)$	15·0	26·4	53·8	123·6	467·0	1294·0

On extra equation is used in the relaxation table to allow more rapid relaxation of any 5 of the 6 columns to reasonable residuals. The equations used for the relaxation process are:

$$F(U) = K_0 + 4 \times 10^{-1}K_1 + 1{\cdot}6 \times 10^{-1}K_2 + 6{\cdot}4 \times 10^{-2}K_3 + 2{\cdot}56 \times 10^{-2}K_4 - 15{\cdot}0 \tag{49}$$

$$F(V) = K_0 + 5 \times 10^{-1}K_1 + 2{\cdot}5 \times 10^{-1}K_2 + 1{\cdot}25 \times 10^{-1}K_3 + 6{\cdot}25 \times 10^{-2}K_4 - 26{\cdot}4 \tag{50}$$

$$F(W) = K_0 + 7 \times 10^{-1}K_1 + 4{\cdot}9 \times 10^{-1}K_2 + 3{\cdot}43 \times 10^{-1}K_3 + 2{\cdot}4 \times 10^{-1}K_4 - 53{\cdot}8 \tag{51}$$

$$F(X) = K_0 + K_1 + K_2 + K_3 + K_4 - 123{\cdot}6 \tag{52}$$

$$F(Y) = K_0 + 1{\cdot}5K_1 + 2{\cdot}25K_2 + 3{\cdot}375K_3 + 5{\cdot}062K_4 - 467{\cdot}0 \tag{53}$$

$$F(Z) = K_0 + 2K_1 + 4K_2 + 8K_3 + 16K_4 - 1294{\cdot}0 \tag{54}$$

The operations table for this set of equations is:

	$\Delta F(U)$	$\Delta F(V)$	$\Delta F(W)$	$\Delta F(X)$	$\Delta F(Y)$	$\Delta F(Z)$
$\Delta K_0 = 1$	1	1	1	1	1	1
$\Delta K_1 = 1$	4×10^{-1}	5×10^{-1}	7×10^{-1}	1	1·5	2
$\Delta K_2 = 1$	$1{\cdot}6 \times 10^{-1}$	$2{\cdot}5 \times 10^{-1}$	$4{\cdot}9 \times 10^{-1}$	1	2·25	4
$\Delta K_3 = 1$	$6{\cdot}4 \times 10^{-2}$	$1{\cdot}25 \times 10^{-1}$	$3{\cdot}43 \times 10^{-1}$	1	3·375	8
$\Delta K_4 = 1$	$2{\cdot}56 \times 10^{-2}$	$6{\cdot}25 \times 10^{-2}$	$2{\cdot}401 \times 10^{-1}$	1	5·0625	16
$\Delta K_1 = \Delta K_2 = \Delta K_3 = \Delta K_4 = 1$	1·65	1·938	2·773	5	13·188	31

The relaxation table used in the solution of these equations is:

	$F(U)$	$F(V)$	$F(W)$	$F(X)$	$F(Y)$	$F(Z)$
K_i's = 0	−15·0	−26·4	−53·8	−123·6	−467·0	−1247
K_i's = 8	−1·8	−10·896	−31·62	−83·6	−361·496	−999
$K_4 = 5 \times 10^1$	−0·52	−7·771	−19·61	−33·6	−108·371	−199
$K_3 = 3 \times 10^1$	+4·28	−0·271	−4·91	−3·6	−40·871	−79
$K_0 = -6$	−1·72	−6·271	−10·91	−9·6	−46·871	−85
$K_2 = 2 \times 10^1$	+1·48	−1·271	−1·11	+10·4	−1·871	−5
$K_0 = -1$	+0·48	−2·271	−2·11	+9·4	−2·871	−6
$K_0 = 1$, $K_1 = 8$, $K_2 = 58$, $K_3 = 8$, $K_4 = 58$	+0·47	−2·275	−2·11	+9·4	−2·88	−6

The original constants reported by HUME *et al.* are $K_0 = 1$, $K_1 = 11$, $K_2 = 56$, $K_3 = 6$ and $K_4 = 60$.

CONCLUSIONS

The relaxation method can be applied in the calculation of successive stability constants in conjunction with the most commonly used experimental methods. It has the advantage of being capable of giving answers even in systems where large numbers of complexes are present and, in fact, it is for such systems that its advantages are seen most forcibly. The ease with which the method can be used in the solution of sets of linear algebraic equations with large numbers of unknowns is an advantage over graphical methods. The method also has the advantages of being a system where the correction of arithmetical errors in the computations is very readily carried out and of allowing a check of the final answer to be easily obtained. The method is superior to the use of determinants in the respect that it is an approximation method and in the respect that any number of equations equal to or greater than the number of unknowns can be used. In working with more equations than unknowns, poor data will not relax as far as good data when the majority of the data is relaxed and this gives an indication of the most suitable points. Perhaps, the major advantage of the method is the speed with which solutions can be obtained.

The relaxation method has the disadvantage, characteristic of most algebraic methods, of treating the equations as exact and is not as flexible as graphical methods in allowing poor data to be selected and discarded. The results obtained are in good agreement with those obtained by other methods. For some systems ill conditioned equations may be encountered. Suggestions for solving such sets have been presented by NEVILLE.[10] FOX[11] has discussed some of the devices which can be used to speed up the relaxation process.

Acknowledgement—This work was supported in part by grants from the Research Corporation and the National Science Foundation.

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J. Inorg. Nucl. Chem., 1961, Vol. 16, pp. 197 to 203. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRON SPIN RESONANCE AND OPTICAL SPECTRA OF CHROMIUM "SANDWICH" COMPOUNDS*

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Abstract—The visible, ultra-violet, and electron spin resonance spectra of the chromium dibenzene cation and similar ions are presented. The hyperfine splittings of 3·5–4·0 G and 20 G are attributed to the hydrogen and chromium-53 nuclei respectively. These spectra are discussed in terms of a molecular orbital theory.

THE unusual configuration[1] of ferrocene type molecules has attracted much attention. The striking properties of these compounds have created much interest in the type of bonding that exists between the metal atom and the other atoms in the complex[2,3,4] Some of the previous studies of "sandwich" molecules include the infra-red spectra,[5] magnetic susceptibility measurements[6] and X-ray structures determinations.[7] It is the purpose of the author to investigate the ground states and some of the excited electronic states of: $[Cr(C_6H_5R)_2]^{0,1+}$

The excited electronic states may be investigated by means of optical spectra. The number, position, and intensity of these bands should give some information as to what types of states are involved in the transitions. The ground state of the compounds which are paramagnetic can be investigated by means of electron spin resonance absorption.

EXPERIMENTAL

The iodide salts of $Cr(C_6H_6)_2^+$ [I], $Cr(C_6H_5D)_2^+$ [II], $Cr(C_6H_6)(C_{12}H_{10})^+$ [III], and $Cr(C_{12}H_{10})_2^+$ [IV] which were used in this investigation were kindly donated by ZEISS[8]. A sample of $Cr(C_6H_6)_2Cl$ [V] was prepared from $Cr(C_6H_6)_2$ [VI], which was obtained from FISCHER[9]. All the salts are soluble to some extent in water, and readily dissolve in ethanol. If the solution is slightly acidic, they are stable for months, when kept in sealed tubes.

Visible and ultra-violet spectra

All the spectra were obtained by using a Cary Model 14 recording spectrophotometer. In all cases, the wavelength scan was 5 Å/sec. The chart drive was 60 or 120 in/hr, and the slit width was $<$0·1 mm except in the region of 2000 Å where a larger slit width was necessitated.

The visible and near infra-red spectrum of I (Fig. 1) consists of a single weak absorption at 11,700 Å ($\epsilon = 7$). Compounds III and IV are similar, having maxima at 12,300 Å ($\epsilon = 10$) and 13,000

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[1] P. F. EILAND and R. PEPINSKY, *J. Amer. Chem. Soc.* **74**, 4971 (1952).
[2] H. H. JAFFEE, *J. Chem. Phys.* **21**, 156 (1953).
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[8] H. H. ZEISS and W. HERWIG, *J. Amer. Chem. Soc.* **78**, 5959, (1956).
[9] E. O. FISCHER and W. HAFNER, *Z. Naturf.* **10 B**, 665 (1955).

Å ($\epsilon = 7$) respectively. This absorption is comparable in position and intensity to the absorptions of other metal ion complexes.[10] There appears to be a slight shoulder on this band. The visible spectrum of VI consists of only one absorption (Fig. 2), which is also of low intensity.

The ultra-violet spectra of I, III, and IV are compared in Fig. 3. There is little difference between the position of the ultra-violet absorptions of these three compounds, but in compounds III and IV there is a marked increase in absorption between 2300 and 2600 Å. The increased absorption in this area by compounds III and IV is attributed to the absorption of the phenyl group, which normally

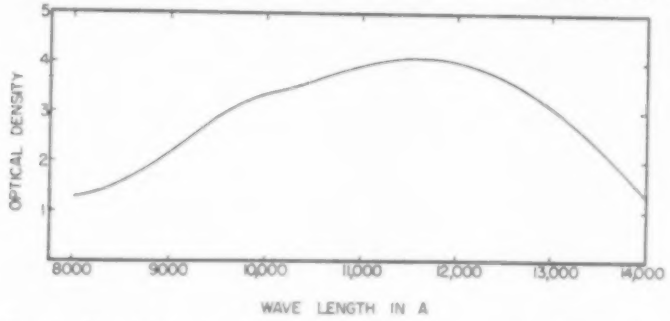

FIG. 1.—Near-infra-red spectrum of chromium dibenzene cation dissolved in water.

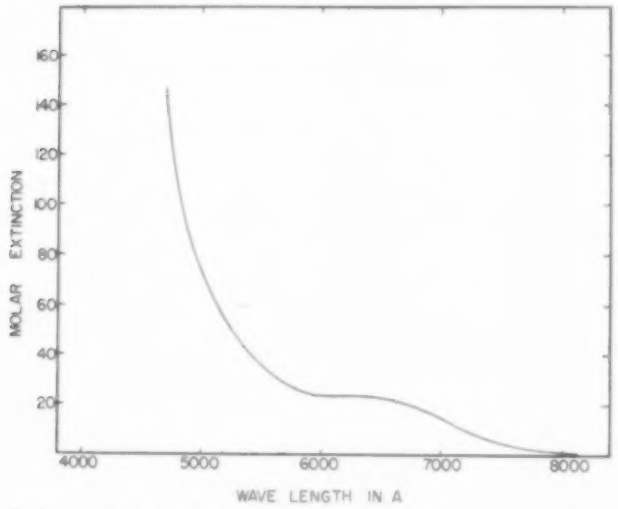

FIG. 2.—Visible spectrum of chromium dibenzene dissolved in cyclohexane.

has absorptions in the region of 2500 Å. In the region down to 2000 Å only one intense absorption was observed for VI at 3200 Å whereas I has three well defined bands in this same region (Fig. 4).

Electron spin resonance

This type of spectra has been well discussed elsewhere.[11,12,13] The spectra were obtained using a transmission cavity spectrometer operating at a frequency of 9·3 kmc/s. All the spectra presented are solution spectra. In all cases where g values were measured, as a reference a small particle of

[10] O. G. HOLMES and D. S. MCCLURE, *J. Chem. Phys.* **26**, 1686 (1957).
[11] B. BLEANEY and K. W. H. STEVENS, *Rep. Progr. Phys.* **16**, 108 (1953).
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[13] J. E. WERTZ, *Chem. Rev.* **55**, 829 (1955).

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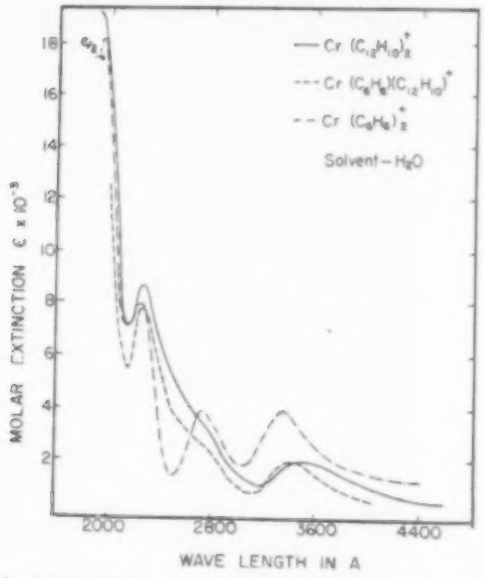

FIG. 3.—Ultra-violet spectra of substituted chromium dibenzene cations.

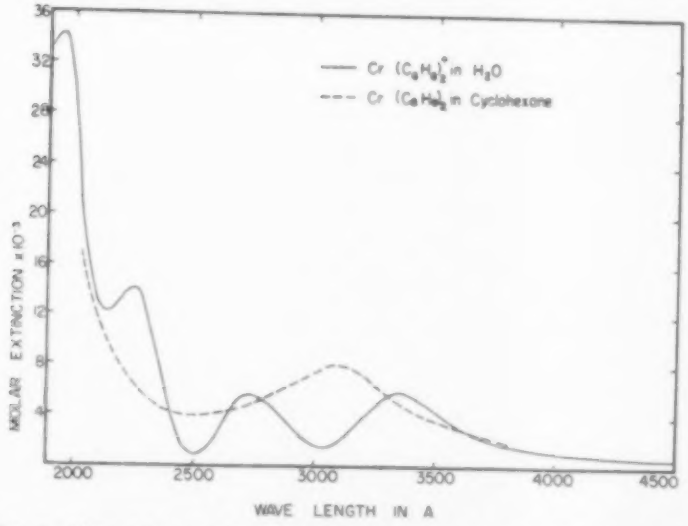

FIG. 4.—Ultra-violet spectrum of chromium dibenzene and chromium dibenzene cation.
$H - H_{2.0036}$ in gauss

1,1-diphenyl-2-picrylhydrazyl was placed in or near the center of the cavity during the measurement.

The monopositively charged chromium bisaromatics are paramagnetic, having one unpaired electron per molecule. Fig. 5 is the spectrum of II in an aqueous solution. There are approximately nine barely resolved lines, as compared with eleven in I.[14] These hyperfine lines are due to the interaction of the electron with the nuclear spins of the hydrogen nuclei. For I, a total of $13(2I + 1)$ lines are expected while the substitution of two deuteriums for two hydrogens should produce an eleven line spectrum. The spectrum of III is quite different from compounds I and II, as seen in Fig. 6.

[14] R. D. FELTHAM, P. SOGO and M. CALVIN, *J. Chem. Phys.* **26**, 1354 (1957).

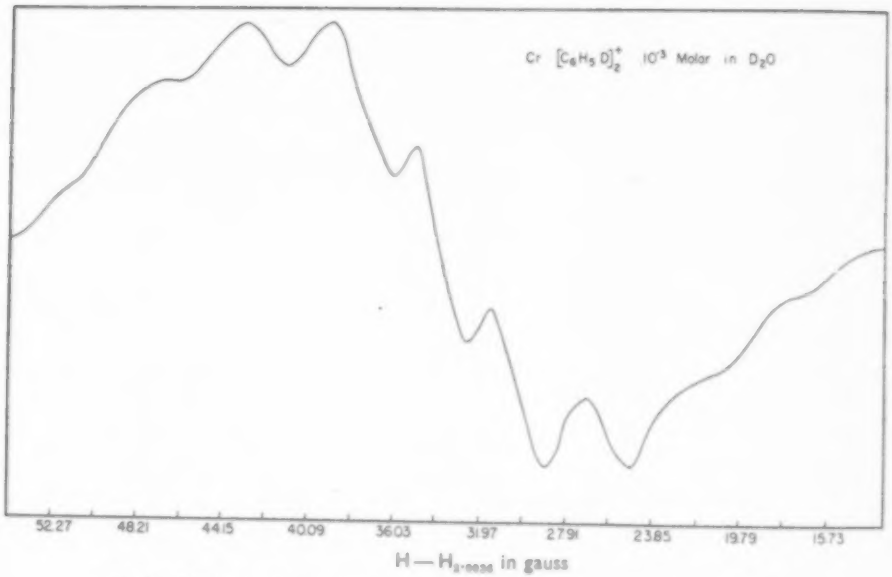

FIG. 5.—Electron spin resonance spectrum of chromium dideuterobenzene cation.

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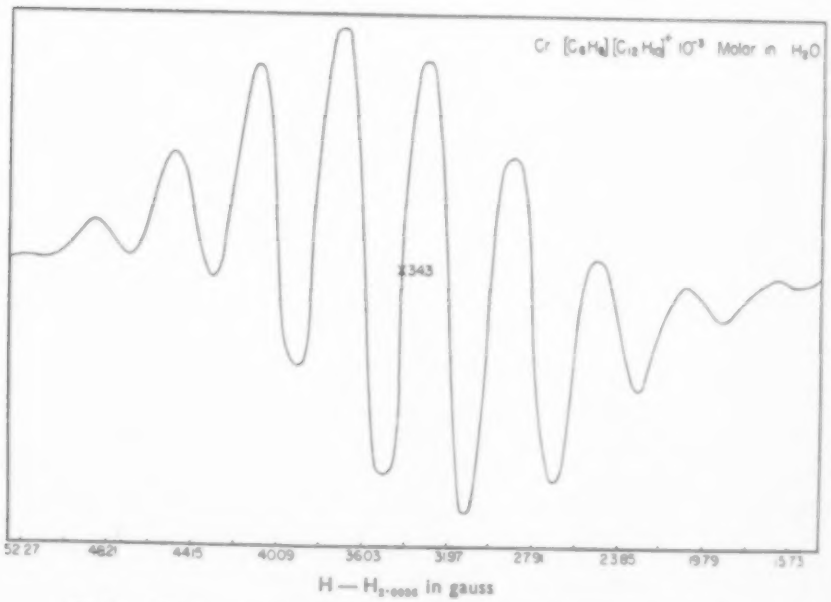

FIG. 6.—Electron spin resonance spectrum of chromium benzene diphenyl cation.

First, the resolution of the lines is much superior; second, there is an even number of lines; and third, the separation between these lines is 4·0 G as compared with a spacing of about 3·5 G for [14]I and II. Since III is the only compound with an odd number of hydrogens, it is the only one of these compounds for which an even number of lines is expected. The g values of all the ions are approximately 1·98. In no case could all the anticipated hyperfine lines be observed, partly because of their low intensity (approximately 1/1000 that of the center lines) and also because of the presence of satellites of moderate intensity.

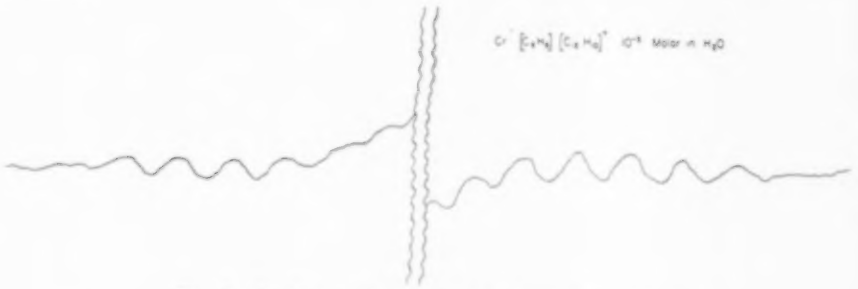

FIG. 7.—Satellites in the electron spin resonance spectrum of chromium benzene diphenyl cation.

In attempting to resolve the theoretical number of lines (12) for III, two satellites were found with an intensity ca. 1/40 that of the more intense spectrum. These satellites overlap the more intense spectrum, as seen in Fig. 7. The separation between the centers of these two satellites is approximately 60 G, and the structure of each satellite is similar to that observed for the more intense spectrum, also having a splitting of 4·0 G.

Of the naturally occurring chromium isotopes only ^{53}Cr (9·5 per cent abundant) has a nuclear spin ($\frac{3}{2}$) and a small magnetic moment. This isotope should give rise to four lines with the same pattern for each of them as is exhibited by the chromium isotopes with no nuclear spin. Assuming that the satellites are due to ^{53}Cr, the hyperfine splitting as calculated from the two observed satellites is approximately 20 G. The hyperfine splitting for ^{53}Cr as observed by Low[15] for Cr^{+3} is 17 G and the intensity relative to the other chromium isotopes is 1/40. There are no other known Cr^{+} complexes with which to compare the g value, but Cr^{3+}, and Cr^{2+} have g values of approximately 1·97.[11] If these satellites arise from the ^{53}Cr isotope, then all of the compounds should possess these satellites. Accordingly all of the compounds were re-examined, and were found to have similar low intensity satellites. IV is quite similar to III except that there are an odd, rather than even number of lines. The superhyperfine structure of the two satellites of IV is well resolved, (not shown), but in all these cases the other two satellites expected for ^{53}Cr were obscured by the more intense spectrum.

A molecule containing ^{13}C (1 per cent abundant) would also be expected to give rise to hyperfine splitting. It can be shown that approximately 10 per cent of the chromium cations would be of the type $Cr(^{12}C_{11}{}^{13}CH_{10})_2^{+}$. Since ^{13}C has a spin of $\frac{1}{2}$, two lines would be expected with an intensity ratio of 18:1 compared to the observed 40:1. The observed splitting is also much too large, the ^{13}C splitting in naphthalene negative ion being only 7·3 G.[16] Molecules containing more than one ^{13}C are present in too small an amount to be considered.

DISCUSSION

In order to discuss the experimental facts, the molecular orbital model of ORGEL[4] will be assumed. This model is derived by assuming that the bonding forces in "sandwich molecules" are of a covalent type. ORGEL specifically treats ferrocene. His treatment will be extended to chromium dibenzene in a later paper (see also Ref.17). Fig. 8 gives the specific results for chromium dibenzene cation. It will be noted that this treatment places the unpaired electron in a bonding d orbital. Since the 3d and 4s

[15] W. LOW, *Phys. Rev.* **105**, 801 (1957).
[16] S. I. WEISSMAN, T. R. TUTTLE and E. DE BOER, *J. Phys. Chem.* **61**, 28 (1957).
[17] R. FELTHAM, UCRL–3867 (1957).

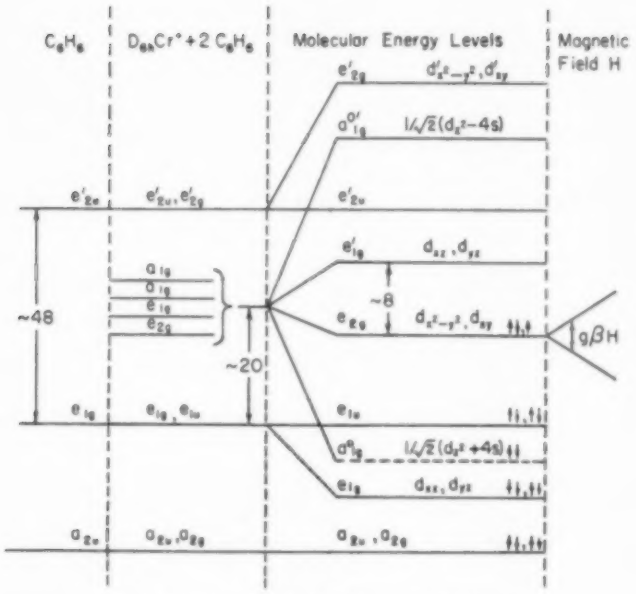

FIG. 8.—Energy levels for chromium dibenzene.

LEGEND
○ denotes non-bonding
/ denotes anti-bonding
denotes bonding
{ denotes degenerate levels
↑ denotes electron

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orbitals of Cr° are approximately degenerate in the free atom, a hybrid orbital $(s - d_z^2)$ has been used as the orbital which bonds with the a_{1g} orbital of the benzene rings. MOFFITT[3] uses this combination to reduce electrostatic energies rather than for improving the bonding of molecular orbitals. Probably both effects are important, but the experimental evidence forces this $a_{1g}{}^{\circ}$ orbital to be of lower energy than the e_{2g} and e_{1g} orbitals. This scheme at least qualitatively agrees with experiment, since it places the electron in an orbital which is a mixture of d orbitals of Cr and p (or $p + s$) orbitals of the carbons. The hyperfine structure together with the observed g values shows this irrefutably.

If one compares the magnitude of the hyperfine splitting to those in benzene negative ion, it is found that the total spread of the hyperfine splitting is twice that in benzene negative ion. MCCONNELL[18] has shown that the magnitude of hyperfine splitting in aromatic free radicals depends upon the exchange integral between the carbon sp^2 hybrid, hydrogen s, and the $\pi(p_z)$ orbitals, and should be directly related to the coefficients of the atomic orbitals that go to make up the molecular orbitals. If the only major difference between the unpaired electron in benzene negative ion and in chromium dibenzene cation is having the molecular orbital composed of a chromium d and carbon p orbital, then one would expect a decrease of the spin density on each of the hydrogens, since one electron would be spread out over two benzene rings and a chromium atom. Since this is not the case, some change must be made in the sigma bonding skeleton of the benzene nuclei. The C—H bond in particular

[18] H. H. MCCONNELL and D. B. CHESNUT, *J. Chem. Phys.* **28**, 107 (1958).

must be affected. This is also reflected in the absence of resolved vibrational structure in the uv absorption bands.

The excited electronic states should also be explained by these molecular orbitals (Fig. 8). There should be one low energy symmetry forbidden transition ($e_{2g} \rightarrow e_{1g}$), and one is found at ca. 8300 cm^{-1} (Fig. 1). The slight shoulder on this absorption may be a spin forbidden transition. There should also be two allowed transitions from the e_{1u} ligand π orbitals to each of the two d orbitals, with an energy separation equal to approximately the energy of the first weak transition. The energy difference found between the first two uv absorptions is 7600 cm^{-1}, which in view of the many assumptions made in this approximation is in excellent agreement with the observed 8300 cm^{-1}. The chromium dibenzene molecule should have only one transition from the e_{1u} to the e_{1g} (compare Fig. 1), and one weak e_{2g}, e_{1g} transition (Fig. 2). The presence of additional phenyl groups in III and IV have only a small effect on the uv spectrum, showing that the bonding between Cr and C is little affected by substituent groups. More information is required to understand other features of the spectra.

Acknowledgements—The author wishes to thank Dr. E. O. FISCHER and Dr. H. H. ZEISS for kindly supplying the compounds used in this investigation, and Dr. P. SOGO for the use of the E.S.R. spectrometer and many helpful discussions on the interpretation of the resonance spectra. I especially want to thank Professor M. CALVIN for his interest and encouragement.

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INFRA-RED ABSORPTION SPECTRA OF TRIMETHYLLEAD CARBOXYLATES; PLANAR STRUCTURE OF $(CH_3)_3Pb^+$

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(*Received* 20 *June* 1960)

Abstract—The infra-red spectra of trimethyllead formate, acetate, and monochloroacetate were examined over the range 400–3500 cm^{-1}. It is shown that these compounds consist of the trimethyllead cation and the carboxylate anion, and that the cation probably has a planar structure.

WHILE many similar properties are observed in the organometallic compounds of the fourth group elements, Si, Ge, Sn, and Pb, there are many different characteristics. One of the most interesting differences is indicated by the infra-red spectra of the carboxylates. In the compounds $(CH_3)_{4-x}Si(OOCCH_3)_x$ ($x = 1$–4), the bond between silicon and acetoxy residue is covalent and similar to the bonding in an organic ester. In the case of trimethyltin carboxylate and dimethyltin dicarboxylate, the bond between tin and carboxylate residue is ionic and similar to the bonding in sodium carboxylate. Thus, these tin compounds should be described more properly as follows:

$$(CH_3)_3Sn^+\left(\begin{matrix}O\\ \diagdown\\ \diagup\\ O\end{matrix}\!\!>CR^-\right) \quad \text{and} \quad (CH_3)_2Sn^{++}\left(\begin{matrix}O\\ \diagdown\\ \diagup\\ O\end{matrix}\!\!>CR^-\right)_2.$$

Further information on the shape of the trimethyltin and dimethyltin cations has been obtained by their infra-red spectra in the KBr region. The results show that the trimethyltin cation and dimethyltin cation probably have a planar and linear configuration,[1] respectively.

This work has been done to extend the above findings to the analogous lead compounds. It has been assumed that the trimethyllead cation, if it exists, would have a planar configuration[2]. In this work, some of the trimethyllead carboxylates were examined by infra-red in the NaCl region, and their spectra show the presence of the trimethyllead cation. Also, the infra-red spectra of these compounds in the KBr region suggest that this cation probably has a planar configuration.

EXPERIMENTAL

Materials. Trimethyllead formate, acetate, and monochloroacetate were prepared directly from tetramethyllead and formic acid, glacial acetic acid and monochloroacetic acid, respectively.[3] The reactions were carried out in an apparatus for sublimation, and the crystals were purified by sublimation at once. Identification was done by their melting points; 114°C (Reported[3]: 113°C) for the formate, 194°C (Reported[3]: 194°C) for the acetate and 167°C (decomposed) (Reported[3]: 167°C) for the monochloroacetate.

[1] R. OKAWARA, D. E. WEBSTER and E. G. ROCHOW, *J. Amer. Chem. Soc.* **82**, 3287 (1960).
[2] R. W. LEEPER, L. SUMMERS and H. GILMAN, *Chem. Rev.* **54**, 150 (1954).
[3] R. HEAP and B. C. SAUNDERS, *J. Chem. Soc.* 2983 (1949).

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Measurements. The infra-red spectra were recorded using a Perkin–Elmer (Model 21) double-beam spectrophotometer equipped with NaCl or KBr optics. In the NaCl region, the spectra were obtained using pressed KBr disks. In the KBr region, Nujol mull and KBr disks were used.

The observed spectrum of trimethyllead formate is shown in Fig. 1 and the vibrational frequencies

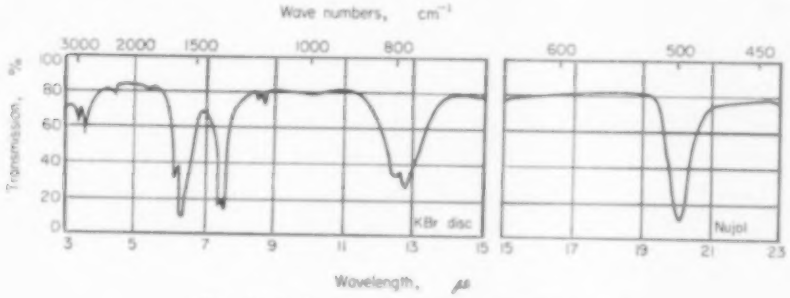

FIG. 1.—Infra-red spectra of trimethyllead formate.

are given in Table 1 together with those of tetramethyllead,[4] trimethyltin formate[1] and sodium formate,[5] which have been reported previously.

The frequencies of trimethyllead acetate and monochloroacetate are listed in Table 2 and 3 with those of trimethyltin and sodium carboxylates.[1]

TABLE 1.—INFRA-RED VIBRATIONAL FREQUENCIES OF THE FORMATES: POSITIONS OF BANDS (IN cm^{-1})

$(CH_3)_4Pb$[4]	$NaOOCH$[5]	$(CH_3)_3SnOOCH$[1]	$(CH_3)_3PbOOCH$	Assignment
478		552	498	M—C asym. str.
765		770 or 790	776 or 797	CH_3(—M) rock.
	784			COO scissor
	1070	—	—	CH out-of-plane bend.
1148		1195	1153	CH_3(—M) sym. str.
		1205	1168	
	1365	1363	1352	COO sym. str.
	1377	1378	1362	CH in-plane bend.
1448		—	—	CH_3(—M) asym. def.
	1620	1590	1580	COO antisym. str.
		1615	1640	

DISCUSSION

The spectra of trimethyllead formate, acetate and monochloroacetate could be interpreted as superpositions of the absorptions of the carboxylic acid anion and those of the trimethyllead cation. Assignment of the bands, as shown in Tables 1–3, can be made by referring to the spectra of tetramethyllead, sodium carboxylate and trimethyltin carboxylate.

The assignment of the bands in the NaCl region, 700–2000 cm^{-1}, can be made with certainty. A strong band associated with methyl group attached to metal atom,

[4] E. R. LIPPINCOTT and M. C. TOBIN, *J. Amer. Chem. Soc.* **75**, 4141 (1953).
[5] R. NEWMAN, *J. Chem. Phys.* **20**, 1663 (1952). See also, T. MIYAZAWA, *J. Chem. Soc. Japan* **77**, 381 (1956) (in Japanese), and H. J. BERNSTEIN, *Canad. J. Chem.* **34**, 170 (1956).

Table 2.—Infra-red vibrational frequencies of the acetates: positions of bands (in cm^{-1}): R = $OOCCH_3$

NaR[6]	$(CH_3)_3SnR$[1]	$(CH_3)_3PbR$	Assignment
460	497	485	COO rock.
	555	499	M—C asym. str.
616	618	581	COO out-of-plane bend.
647	664	658	COO scissor
	775	781	CH_3(—M) rock.
		794	
923	940	928	CC str.
1007	1015	1010	CH_3 rock.
1045	1048	1043	
	1194	1153	CH_3(—M) sym. def.
	1206	1168	
1339	1352	1339	CH_3 sym. def.
1425	1428	1408	COO sym. str.
1440			CH_3 asym. def.
1484			
1582	1576	1560	COO antisym. str.

CH_3(—M), is found at 770–800 cm^{-1} in the lead and tin compounds shown in Tables 1–3. In trimethyltin compounds, this band has been assigned[1] to the rocking vibration of the methyl group. In lead compounds, this band can be assigned to the same vibration with reference to the assignment of tetramethyllead. In the formate the absorption due to the COO scissors, and in the monochloroacetate that of the C—Cl stretching fall in this region. The symmetric deformation vibrations of methyl

Table 3.—Infra-red vibrational frequencies of the monochloroacetates: positions of bands (in cm^{-1}): R = $OOCCH_2Cl$

NaR[6]	$(CH_3)_3SnR$	$(CH_3)_3PbR$	Assignment
429	501	470	COO rock,
	556	496	M—C asym. str.
576	—	—	COO out-of-plane bend.
670	678	634	COO scissor
770	765 or 783	778 or 798	CCl str.
			CH_3(—M) rock.
926	—	—	CC str.
933	938	938	CH_2 rock.
	1196	1153	CH_3(—M) sym. def.
		1166	
1166	—	—	CH_2 twist.
1248	1250	1250	CH_2 wag.
1399	1393	1390	CH_2 scissor
1425	1418	1415	COO sym. str.
1595	1640	1600	COO antisym. str.
		1620	

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groups attached to silicon, germanium and tin show one or two sharp bands near 1260, 1230 and 1200 cm^{-1},[6] respectively; in the three trimethyllead compounds studied here, two sharp bands at 1153 and 1168 cm^{-1} can be assigned to this vibration. Another band attributable to the asymmetric deformation vibration, found at 1448 cm^{-1} in tetramethyllead, is hidden in the carboxylate. All the other bands can be readily assigned to the carboxylate anion, by comparing the bands with those of sodium carboxylate and trimethyltin carboxylate. A few weak bands found in sodium carboxylate do not appear in the spectra of the lead and tin compounds under these experimental conditions.

From the spectra in the KBr region, it is possible to obtain some information about the shape of the trimethyllead cation. One of the authors has already shown that trimethyltin formate has in this region only one absorption which is to be assigned to the Sn—C asymmetric stretching vibration. And it was concluded that the trimethyltin cation has a planar structure from the standpoint of infra-red spectra.[1] A similar phenomenon is observed in the present work. In the spectrum of trimethyllead formate only one band appears in this region. Since the formate anion shows no bands below 700 cm^{-1}, this band must be due to the trimethyllead cation. If the cation has a planar structure, the symmetric stretching vibration must be infrared inactive, and only the Pb—C asymmetric stretching vibration can be expected in this region. This assignment in the KBr region is further supported by the frequency of the band. In the case of tetramethyltin, trimethyltin formate, and dimethyltin diformate the band assigned to the Sn—C asymmetric stretching vibration is found at 528 cm^{-1}, 552 cm^{-1} and 592 cm^{-1}, respectively. A similar shift to a higher frequency is observed in the case of tetramethyllead and trimethyllead formate. In trimethyllead acetate and monochloroacetate, one strong band appears in almost the same position as in the case of the formate, and this can be assigned to the Pb–C asymmetric vibration, if the other bands can be assigned to the carboxylate anion as given in Tables 2 and 3.

[6] M. P. Brown, R. Okawara and E. G. Rochow, *Spectrochim. Acta* 16, 595 (1960).

J. Inorg. Nucl. Chem., 1961, Vol. 16, pp. 208 to 212. Pergamon Press Ltd. Printed in Northern Ireland

"ONIUM" BASE BOROHYDRIDES—II

SOME PHENYL COMPOUNDS

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Abstract—The new borohydrides of the tetraphenyl phosphonium, triphenyl sulphonium and diphenyl iodonium cations are described, and an account is given of the thermal decomposition of the first named, which gives rise to the previously unreported triphenyl phosphine–borine co-ordination compound.

THE first paper of this series[1] described the preparation and thermal decomposition of the rather unstable trimethyl sulphonium borohydride. The present paper deals mainly with the preparation and thermal decomposition of tetraphenyl phosphonium borohydride, and also gives preliminary information on triphenyl sulphonium borohydride and diphenyl iodonium borohydride. None of these phenyl compounds has previously been described. As before, the method of preparation employed was in all cases a simple metathesis in cold aqueous solution between the fluoride of the "onium" base and an alkali borohydride. The fluorides were chosen because most of the other common salts are insufficiently soluble in water. All three of the phenyl "onium" borohydrides are sparingly soluble, and precipitate readily from the reaction mixture. Their thermal decomposition conforms in part to the pattern already established for "onium" tetraphenyl borates[2] and for trimethyl sulphonium borohydride,[1] in which a molecule of hydrocarbon is eliminated between cation and anion; but there are competing reactions in which polymer is formed.

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EXPERIMENTAL

Tetraphenyl phosphonium (TP) *borohydride*

TP bromide was prepared as described by WILLARD *et al.*[3] The crude bromide dihydride was recrystallized twice from methanol. The yields of purified product from two preparations (16 g and 15 g) fell far short of the 50 g of crude product reported in the original work. (Found: C, 63·7; H, 5·63. Calc. for TP bromide dihydrate. C, 63·3; H, 5·31%).

In a typical preparation, 7·26 g (15·95 mmole) of TP bromide dihydrate were dissolved in the minimum of water (about 400 ml) at room temperature. The solution was run slowly through a column containing 50 ml of well washed Amberlite IRA-400 anion exchange resin in the fluoride form. The effluent still contained about 10 per cent of the bromide ion originally present. The effluent and washings were concentrated to 65 ml at room temperature in a rotary film evaporator. To the resulting solution, at 0°C, was added a cold solution of 0·896 g (15·95 mmole) of recrystallized potassium borohydride in 8 ml water. TP borohydride precipitated immediately as small, colourless needles. It was filtered with suction on a sintered glass funnel jacketed with ice-cold water, and washed with three small portions of ice-cold water. Without delay the funnel and precipitate were transferred to a desiccator containing concentrated sulphuric acid desiccant, which was evacuated. Yield of dry TP borohydride 4·7 g (83 per cent). (Found: C, 79·5; H, 7·15;

[1] H. G. HEAL, *J. Inorg. Nucl. Chem.* **12**, 255 (1960).
[2] G. A. RAZUVAYEV and T. G. BRILKINA, *Dokl. Akad. Nauk SSSR* **85**, 815 (1952).
[3] H. H. WILLARD, L. R. PERKINS and F. F. BLICKE, *J. Amer. Chem. Soc.* **70**, 737 (1948).

P, 7·7, 8·5; B, 3·04, 3·05. Calc. for $(C_6H_5)_4PBH_4$: C, 81·4; H, 6·83; P, 8·7; B, 3·05%). Volume of hydrogen evolved on treatment with excess 6 N hydrochloric acid; 98·8, 100·9 per cent of theoretical for the reaction

$$BH_4^- + H^+ + 3H_2O \rightarrow H_3BO_3 + 4H_2.$$

The solubility of TP borohydride in chloroform was estimated by weighing the residue from evaporation of weighed samples of solution saturated at 0°C. Solutions in water and in ethanol decomposed too rapidly, with evolution of gas, to give reliable solubility values by this method, but the solubility in water was estimated from the percentage yield in the preparation.

TP borohydride was thermally decomposed in an apparatus like that described previously.[1] In a typical run, 2·17 g (6·11 mmoles) of freshly prepared material were decomposed *in vacuo* at 185–210°C, and the residue heated in high vacuum for a further 1½ hr at 190–230°. 0·1 mmole of gas not condensible at −196°, presumably hydrogen, was produced. The other volatiles evolved during decomposition and subsequent heating consisted almost entirely of 0·206 g (2·64 mmole) of nearly pure benzene. This was identified by its melting point (4–6°C), vapour-pressures (4 per cent above literature values between 3·8°C and 13·9°C), vapour density (giving mol wt. 77·1, theory 78·1), and by its infra-red spectra in the liquid and vapour states, which were indistinguishable from those of pure benzene. It smelled, however, of boron hydrides.

In the top of the reaction vessel 1·60 g of a white sublimate collected. It consisted of high-melting crystals X mixed with a low-melting substance Y. A partial separation was effected by extraction with ethyl ether, in which Y was much more soluble than X. Two 10 ml portions of ether extracted 0·40 g of material melting over the range 50°–70°C. This was recrystallized twice from methanol, with considerable losses owing to the high solubility of the Y, and the presence of much X. This gave 0·02 g of pure Y. It was identified as *triphenyl phosphine* by the melting point (Found: 77°C; literature value[4] 76°C) and by analysis. (Found: C, 82·6; H, 5·6; P, 10·4; Calc. C, 82·4; H, 5·8; P, 11·8%). The part of the sublimate which had not dissolved in ether was now extracted with 25 ml of hot benzene. It dissolved, except for 0·11 g of white material thought to be undecomposed TP borohydride which had been thrown into the upper parts of the reaction vessel during the decomposition. The benzene solution was evaporated, and the residue recrystallized from benzene. 0·42 g of colourless needles of X resulted. These melted sharply at 188° (uncorr.). X was identified as *triphenyl phosphine–borine*; $(C_6H_5)_3P{\cdot}BH_3$. (Found: C, 78·5; H, 6·4; P, 9·9, 12·0; B, 3·6, 3·6. Calc. C, 78·3; H, 6·6; P, 11·2; B, 3·9%. Mol. wt. Found: 274, 280; Calc. 276).

The residue in the bottom of the reaction vessel was a brown resin which gave the analysis: C, 78·8; H, 8·1; B, 6·9, 7·0; P, 6·1%. It dissolved partially in benzene, the benzene extract leaving a viscous liquid on evaporation. The portion insoluble in benzene was green and flocculent while wet with benzene, and dried to a free-flowing light brown powder, which gave the analysis: C, 48·6, 49·8; H, 6·7, 6·7; P, 1·2; B, 7·3, 7·4%.

In four thermal decompositions the products were always obtained in approximately the proportions just described.

Triphenyl sulphonium (TS) *borohydride*

This compound[5] was prepared from the bromide in exactly the same way as TP borohydride. Its solubilities and thermal decomposition were similarly investigated.

Diphenyl iodonium (DI) *borohydride*

This compound was similarly prepared. It proved to be much less stable than the other two borohydrides. The crystals were dried by transferring them to a bulb which was immersed in ice-water and kept highly evacuated for several hours. They were not analysed, since the compound detonated violently at room temperature about a minute after air was admitted to the bulb. *In vacuo* it appeared to be stable at room temperature. It decomposed *in vacuo* at about 110° with a weak explosion which did not break the container, and the decomposition products were worked up as described for TP borohydride.

[4] J. R. Van Wazer, *Phosphorus and its Compounds* Vol. 1, p. 194. Interscience, New York & London (1958).
[5] H. G. Heal and J. A. B. Martin. To be published.

Solvents

Ether and benzene had stood over sodium for some time and were distilled from fresh sodium immediately before use. Chloroform was purified using the method described by GROSS and SAYLOR[6], dried over calcium sulphate followed by phosphorus pentoxide and distilled immediately before use.

Infra-red spectra

Infra-red spectra were taken with a Perkin–Elmer Infracord machine.

Molecular weight

Molecular weight determinations were made ebullioscopically in benzene solution, using the BOBRANSKI–SUCHARDA semi-micro apparatus.[7]

Analysis

Carbon and hydrogen were usually determined by the normal dry combustion method. This tends to give low carbon results with boron compounds, but since most of the samples contained eighteen to twenty-four carbon atoms to one boron atom the error could not, in the worst circumstances, be large. In the case of the second analysis of the resin quoted above, the total percentages fell far short of 100 per cent and the carbon figure was checked by wet combustion as described by LINDENBAUM *et al.*[8] The values obtained were almost the same as the dry combustion values quoted.

For boron determinations, the borohydrides were decomposed simply by dissolving them in dilute hydrochloric acid. Triphenyl phosphine–borine was decomposed by fusion with anhydrous sodium carbonate.[9] The resin was also treated in this way but, in a check determination, one sample was heated to 460° for 15 min with calcium hydroxide in a sealed silica tube[9] in order to ensure complete decomposition without loss of volatile boron compounds. The result agreed with those obtained by sodium carbonate fusion. The final stage of the boron determinations was always titration of boric acid in presence of mannitol.

For the determination of phosphorus, the samples were broken down in the conventional way with fuming nitric acid in a Carius tube, and the phosphorus precipitated and weighed as ammonium phosphomolybdate. With TP borohydride, heating to the usual temperature of 320°C did not decompose the sample completely and, instead, the tubes were heated at 380–400°C for an hour. Some of the phosphate formed adhered to the glass, which was slightly attacked, and this was removed by extracting with hot sodium carbonate solution. A blank determination was performed in this case.

RESULTS AND DISCUSSION

Tetraphenyl phosphonium borohydride forms colourless, non-hygroscopic needles. In accordance with its presumably ionic constitution, it is soluble in water (2 g per 100 g at 0°), in chloroform (34 g per 100 g at 0°) and readily soluble in methylene chloride and ethanol, but practically insoluble in benzene, carbon tetrachloride, diethyl ether and ethylene glycol dimethyl ether ("monoglyme"). Its high solubility in chloroform and methylene chloride, a common property of tetraphenyl phosphonium salts, endows it with potentialities as a reducing agent for organic substances which are now being examined in this Department.

On storage in a desiccator, the compound underwent no visible deterioration in months other than a slight darkening of the surface layers in light. However, the yield of hydrogen on treatment with dilute hydrochloric acid fell somewhat below theoretical. From one sample, prepared using recrystallized potassium borohydride

[6] P. M. GROSS and J. H. SAYLOR, *J. Amer. Chem. Soc.* **53**, 1744 (1931).
[7] B. BOBRANSKI and E. SUCHARDA, *Chem. Z.* **52**, 923 (1928).
[8] A. LINDENBAUM, J. SCHUBERT and W. D. ARMSTRONG, *Analyt. Chem.* **20**, 1120 (1948); also D. VAN SLYKE, *Ibid.* **26**, 1706 (1954); **27**, 214 (1955).
[9] HOUBEN-WEYL *Methoden der organischen Chemie* (4th Ed.) Vol. 2, p. 207. Georg Thieme Verlag, Stuttgart (1953).

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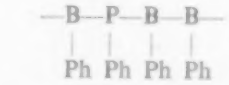
of at least 99 per cent purity, the yield fell to 87·5 per cent of theoretical in only a week's storage at room temperature. From another sample, prepared using potassium borohydride of 97 per cent purity as supplied by Metal Hydrides Inc., the hydrogen yield was still 94 per cent of theoretical even after 3½ months' desiccator storage, of which 1 month was at room temperature and the rest at −10°C. Since oxygen initiates an explosive reaction in the similarly constituted diphenyl iodonium borohydride, we suspect that a slow oxidation (perhaps of BH_4^- to the known ion[10] BH_3OH^-) possibly inhibited by certain impurities, may account for the fall in hydrogen yield.

Analogy with other "onium" borohydrides[1] led us to expect that the thermal decomposition would go according to the equation

$$[(C_6H_5)_4P]^+[BH_4]^- \rightarrow C_6H_6 + (C_6H_5)_3P{\cdot}BH_3$$

one mole of the borohydride giving a mole each of benzene and triphenyl phosphine–borine. Both these compounds did result, but in much less than quantitative yield. Using the data of the run reported above, one mole of borohydride gave 0·45 mole benzene and about the same quantity of triphenyl phosphine–borine. There is no question that the benzene was completely recovered. The other major volatile product was triphenyl phosphine. The yield is difficult to estimate exactly, but was probably not less than 0·17 mole and certainly not greater than 0·25 mole. Since practically no boron hydrides were present in the products, it is unlikely that the triphenyl phosphine resulted from dissociation of triphenyl phosphine–borine formed primarily, for this would have given some diborane and other hydrides from pyrolysis of diborane. The remaining decomposition product was the resin. One might have expected this to consist of a boron-phosphorus skeleton with phenyl groups attached, but neither the analyses nor the infra-red spectrum agree with such a constitution. A polymer of structure such as



with trivalent boron and phosphorus atoms in random alternation, would need to have at least one atom of (B + P) for every phenyl group, if linear, or more if branching were allowed for. The analysis shows only 0·73 atoms (B + P) per six atoms of carbon. The infra-red spectrum (in a potassium bromide disk, prepared under nitrogen) was complex and poorly resolved. The aromatic C—H stretching frequency at about 3000 cm^{-1} was very weak. There was a strong absorption at 2900 cm^{-1}, which does not correspond to P—H or B—H frequencies, and most probably arose from an aliphatic C—H stretching vibration. The evidence seems to suggest that there had been ring opening, probably catalysed by the Lewis acid BH_3 which must have existed in the reaction zone, and that the resin had, at least in part, a carbon skeleton. There was practically no absorption between 1800 and 2700 cm^{-1}, which includes the B—H stretching region, implying the absence of BH or BH_2 groups. The analyses for C, H, B and P of the resin which had been crushed and extracted with benzene fall short of 100 per cent by 35·5 per cent. There is no possibility of any error of this order of magnitude, and the deficiency must be attributed to oxygen picked up

[10] J. Goubeau and H. Kallfass, *Z. Anorg. Chem.* **299**, 160 (1959).

during the treatment. Supporting this explanation, there was a strong absorption in the I.R. spectrum of this material at 3250 cm^{-1}, the O—H stretching region, which was missing from the spectrum of the untreated resin.

The compound *triphenyl phosphine–borine*, forming needles of m.p. 188° (uncorr.), which has just been mentioned as a major decomposition product, has not previously been reported. It appears to be extremely stable, being unaffected by moist air, and insoluble in, and unaffected by, water, 2 N sodium hydroxide or 6 N hydrochloric acid. It is sparingly soluble in ether and readily soluble in benzene, the solubility increasing markedly with temperature in both solvents.

To summarize, the decomposition appears to involve nucleophilic displacement of triphenyl phosphine from the cation by the anion, leading to the formation of benzene and BH_3, the latter uniting with the triphenyl phosphine to give the stable co-ordination compound. This is accompanied by extensive polymer formation. Whether the polymer is formed directly from TP borohydride, or secondarily by decomposition of the triphenyl phosphine–borine, will, it is hoped, become clear after an examination of the pyrolysis of triphenyl phosphine–borine which is being undertaken here.

TS borohydride is rather less stable than TP borohydride (decomposition temperature 160°C as compared with about 190°C), and DI borohydride (decomp. 110°C *in vacuo*) still less stable. This is not surprising, since less symmetrical structures and charge distributions in the cation would probably facilitate nucleophilic attack. Our preliminary results indicate a general mode of thermal decomposition of TS and DI borohydrides very much like that found for TP borohydrides. In all three cases the yield of benzene is less than half the theoretical for the simple nucleophilic displacement reaction, and much polymer is formed. However, diphenyl sulphide and iodobenzene appear as such in the products, and not as co-ordination compounds with BH_3, since these co-ordination compounds, in contrast to triphenyl phosphine–borine are, not stable.

The contrast between the feeble explosion with which DI borohydride decomposes *in vacuo*, and the shattering detonation produced by admitting air to it, is curious, and seems to imply two different chain mechanisms.

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THE DIRECT SYNTHESIS OF ORGANOARSENIC AND ORGANOANTIMONY COMPOUNDS

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Abstract—The convenient preparation of some methyl, ethyl, vinyl and phenyl halo-arsines and -stibines by the action of the corresponding hydrocarbon halides on elementary arsenic and bismuth is described. Suitable conditions vary with the halide employed: methyl bromide and chloride react satisfactorily at 350–375° in the presence of copper as catalyst, but vinyl bromide and chloride require a temperature at least 100° above this. Methyl iodide reacts at 280°, but the yields are poor. Silver is a superior catalyst for the reaction of bromobenzene with arsenic. Bismuth gave no isolable product with methyl chloride, but methyl bromide gave a low yield of methyldibromobismuthine.

THE action of methyl chloride upon elementary silicon,[1] germanium[2] and tin,[3] usually in the presence of a suitable catalyst, produces organometallic chlorides of the type $(CH_3)_nMCl_{4-n}$, where M represents the Group IVb element used. Other hydrocarbon halides show related reactions. The elements of Group Vb are quite different in general behaviour, however, and there is no assurance that a similar approach to organometallic derivatives could be used. Although AUGER[4] found that methyl iodide reacted with precipitated arsenic, and EMELÉUS *et al.*[5] have used the reaction of iodotrifluoromethane with arsenic and antimony to prepare derivatives of these elements, no general study of the reaction of hydrocarbon halides with arsenic, antimony and bismuth seems to have been made. This paper indicates that the direct reaction is a practicable method of synthesis, although it is limited in its applicability.

EXPERIMENTAL

The general procedure was to pulverize "metallic" arsenic (or antimony or bismuth), mix in the desired proportion of catalyst (if any), and then to support the powder on convolutions of glass wool or on masses of asbestos* within a glass tube 20–25 mm i.d. and 70 cm long. With a stream of hydrogen flowing through it, the tube was heated in an electric furnace to 350°, and then the hydrogen was shut off and a slow stream of the desired hydrocarbon halide was sent through the tube. The temperature was adjusted to the desired value, and the reaction kept running for the number of hours or days required. In most experiments no attempt was made to exhaust the charge. Chloro- and bromobenzene were carried into the reaction tube by a stream of nitrogen bubbling through the warm liquid. The condensed reaction products were fractionally distilled, where possible; if decomposition was too extensive, the crude reaction product was alkylated with n-BuMgBr and the

* As will be realized by anyone who has conducted such experiments, the finely-divided powder cannot be packed solidly in a tube without setting up prohibitive resistance to flow of gases. Some form of dispersed support therefore is necessary, and it must be arranged to avoid channeling. Since no supporting material can be considered inert at 370° in such reaction, the choice of material may be expected to influence the reaction. Such effects were explored, in part, and the results appear in Table 1. Some of the reaction temperatures, of course, were too high to be sustained by glass wool.

[1] E. G. ROCHOW, *J. Amer. Chem. Soc.* **67**, 963 (1945).
[2] E. G. ROCHOW, *J. Amer. Chem. Soc.* **67**, 1729 (1947).
[3] A. C. SMITH and E. G. ROCHOW, *J. Amer. Chem. Soc.* **75**, 4103, 4105 (1953).
[4] V. AUGER, *C.R. Acad. Sci., Paris* **145**, 809 (1907).
[5] H. J. EMELÉUS, R. N. HASZELDINE and E. G. WALASCHEWSKI, *J. Chem. Soc.* 1952 (1953).

mixed alkyls vacuum distilled. Products were identified by boiling point, index of refraction, and analysis.*

Copper-catalysed reaction of methyl chloride with arsenic

A 21 mm glass tube was charged with 57 g of pulverized arsenic and 10 g of copper powder, and the mixture was heated to 350° in an atmosphere of hydrogen for 3 hrs. The hydrogen then was replaced by methyl chloride, introduced at a rate of 7 cm³/min (volume at room temperature). The reaction products were collected in an ice-cooled trap attached to the tube by means of a ground-glass joint. Over an interval of 170 hr the yield of liquid products was 30 g. In addition to this, 1·17 mg of white crystals were isolated, but they could not be identified.

Repeated distillation of the liquid products yielded a colourless liquid boiling at 129°. It was thought to be pure CH_3AsCl_2, but analysis showed that it contained $(CH_3)_2AsCl$. (Found: C, 8·37; H, 2·09; Cl 41·43. Calc. for CH_3AsCl_2: C, 7·45; H, 1·88; Cl, 44·08%). As it was not possible to separate the reaction products by means of further fractional distillation, the product was butylated with n-C_4H_9MgBr, hydrolysed with a solution of ammonium chloride, and then again fractionally distilled. The fractions were:

(1) $(CH_3)_2AsC_4H_9$, b.p. 32°/16 mm (Found: C, 46·99; H 9·81. Calc. C, 44·46; H, 9·33%). This fraction contained hydrocarbon impurities which could not be separated, so the product was isolated from this fraction as the CH_3I adduct $(CH_3)_2C_4H_9AsI$. (Found: C, 27·88; H, 6·08; I, 41·68. Calc. C, 27·65; H, 5·96; I, 41·75%). The yield was 10·6 g and corresponds to 4·9 g of $(CH_3)_2AsCl$ (20·2 per cent).

(2) $CH_3As(C_4H_9)_2$, b.p. 75°/10 mm (Found: C, 52·88; H 10·18. Calc. C, 52·94; H, 10·37%). The yield was 24·5 g corresponding to 19·3 g of CH_3AsCl_2 (79·8 per cent).

A similar experiment was carried out in which the contact mass was supported on asbestos. Over an interval of 50 hr the yield of liquid reaction products was 56 g. The crude product comprised 17·3% $(CH_3)_2AsCl$ and 82·7% CH_3AsCl_2.

Reaction of methyl bromide with arsenic

Similar experiments were carried out in which methyl bromide was passed over heated arsenic powder, both with and without copper as catalyst, at various temperatures. The conditions and the results are summarized in Table 1.

Two further experiments are reported in detail in order to contrast the effects of glass surface vs. that of asbestos:

(A) A mixture of 83% As and 17% Cu was supported on asbestos and was heated in H_2 to 360° for 3 hr. Methyl bromide was then introduced at a rate of 36·5 g/hr. Over an interval of 10 hr the yield of liquid reaction products was 98 g. The products were fractionally distilled, yielding three fractions:

(1) b.p. 64–120°/714 mm, 3 g of fore-run, or 3·6 per cent;

(2) b.p. 126–131°/714 mm, 27 g $(CH_3)_2AsBr$, or 32·5 per cent;

(3) b.p. 176–182°/714 mm, 53 g CH_3AsBr_2, or 63·9 per cent.

Fractions (2) and (3) were redistilled under reduced pressure, yielding:

(a) $(CH_3)_2AsBr$, b.p. 51°/42 mm, nearly colourless liquid, d_4^{25} 1·9053, n_D^{20} 1·6813. (Found: C,13·15;H, 3·17; Br, 43·27; Calc. C, 12·99; H, 3·27; Br 43·22%).

(b) CH_3AsBr_2, b.p. 89°/41 mm, oily, pale yellow liquid, d_4^{25} 2·6588, n_D^{20} 1·6808. (Found: C, 5·05; H, 1·23; Br, 64·1. Calc. C, 4·81; H, 1·21; Br, 64·0%).

Ten grammes of white crystals which were obtained from the reaction tube were recrystallized from alcohol and ether, and were found to be the addition compound of CH_3Br with the two methyl bromoarsines. They decomposed at 120–140° with the evolution of methyl bromide.

(B) A similar mixture of pulverized arsenic and copper was supported on 5 g of glass wool and heated to 360°. Methyl bromide was introduced at a rate of 48 g/hr. Over an interval of 10 hr the yield of liquid reaction products was 230 g. The products were fractionally distilled, yielding

(1) b.p. 64–120°/717 mm, 5·5 g of fore-run, or 3·3 per cent;

(2) b.p. 126–131°/717 mm, 54·5 g of $(CH_3)_2AsBr$, or 33·8 per cent;

(3) b.p. 176–182°/717 mm, 100 g of CH_3AsBr_2 or 62·5 per cent.

* Microanalyses were performed by A. PEISKER-RITTER, Microanalytical Laboratory, Brugg, Switzerland, and by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

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TABLE 1

	Temp. (°C)	CH_3Br used in 10 hr (g)	Yield in g/hr	Fore-run(%)	$(CH_3)_2AsBr$(%) b.p. 129–130°C	CH_3AsBr_2(%) b.p. 180–181°C	$AsBr_3$(%) b.p. 210–216°C
1	250	81	0·75				
2	280	103	0·7	4	21·8	74·2	—
3	300	167	3·05				
4	320	84	3·15	5·1	27·6	67·3	—
5	340	120	5·3				
6	360	158	9·8	3·6	32·5	63·9	—
7	370	177	9·8	4	24	72	—
8	370	266	13·9	3·5	37·7	58·8	—
9	370[a]	165	6·6	1	33·7	65·3	—
10	370[b]	158	6·6	1	42[e]	57[e]	—
11	370[c]	385	22·5	2·3	22·6	75·1	—
12	370[d]	198	6·9	1·4	14·8	70	13·8
13	380	—	13·8	1	18·3	68·5	12·2
14	380	—	9·25	1	25·6	70·6	2·8
15	400	170	13·3	3·3	14·4	57·5	24·8
16	420	154	15·2	2·9	3·6	53·3	40·2
17	440	270	12·8	1·1	5·6	52·3	41·0

[a] No catalyst was used.
[b] No catalyst was used, and the introduced CH_3Br was not recycled.
[c] Cu was used as a catalyst, but the introduced CH_3Br was not recycled.
[d] No catalyst was used, but HBr was added to the introduced CH_3Br.
[e] These are the average results of five runs under identical conditions.

From the amounts of CH_3Br used and recovered, it was found that 28 per cent of the CH_3Br consumed was converted to methyl bromoarsines. The other 72 per cent of the CH_3Br was pyrolysed at this temperature to give H_2, C, HBr and other products. The unchanged CH_3Br recovered from this experiment contained 5% HBr, vs. 20 per cent in the previous experiment using asbestos.

From these two runs and the previous ones, it may be concluded that glass wool is a more satisfactory support than asbestos.

Copper-catalysed reaction of methyl iodide with arsenic

The uncatalysed liquid-phase reaction of methyl iodide with arsenic in a sealed tube has been described before,[6] but the yields of methyl iodoarsine were poor and the chief product was AsI_3. We heated a mixture of 10 g of arsenic and 2 g of copper with 50 g of methyl iodide in a sealed tube to 100° for 18 hr and found no reaction. We then tried heating arsenic (either with or without copper) with methyl iodide to 150° and to 200°, but obtained mostly arsenic triiodide and only a few drops of liquid assumed to be methyl iodoarsine. Finally, from 10 g of arsenic and 50 g of methyl iodide in a sealed tube at 200° for 18 hr there was obtained arsenic triiodide and a small amount of solid melting at 175–179° containing 62·1% I.

The heterogeneous gas–solid reaction of methyl iodide with arsenic at 280° and one atmosphere was more successful. Fifty grammes of pulverized arsenic and 10 g of copper were mixed and heated

[6] L. MAIER, D. SEYFERTH, for $(CH_2{=}CH)_2AsBr$, 59°/19 mm; for $CH_2{=}CHAsBr_2$, 74–76°/14 mm. F. G. A. STONE and E. G. ROCHOW, *J. Amer. Chem. Soc.* **79**, 5884 (1957).

for 3 hr at 350° in a stream of hydrogen, and then the temperature was reduced to 280° and the vapour of methyl iodide was introduced at a rate of 10 g/hr carried by nitrogen. After 50 hr 6·2 g of liquid product collected in the ice-cooled trap. From its iodine content, the product appeared to be a mixture of 90% CH_3AsI_2 (73·8% I), and 10% $(CH_3)_2AsI_2$ (54·71% I). Thus the conversion was small, but no AsI_3 was obtained. A higher concentration of methyl iodide, injected into the reaction tube without nitrogen carrier by using a proportioning pump, might have been beneficial.

Copper-catalysed reaction of ethyl chloride with arsenic

A mixture of 40 g of arsenic powder and 8 g of copper was heated in a reaction tube to 340°, and ethyl chloride was introduced at a rate of 3 cm³ of gas per minute at room temperature. Over an interval of 120 hr 2·3 g of liquid products were obtained. Fractional distillation gave a colourless liquid, b.p. 48–50°/64 mm. The chlorine content was 23·09 per cent, which lies between that of $(C_2H_5)_2AsCl$ (21·04 per cent) and that of $C_2H_5AsCl_2$ (40·55 per cent). These data indicate that the principal product was diethylchloroarsine, $(C_2H_5)_2AsCl$, formed in low yield.

Silver-catalysed reaction of chlorobenzene with arsenic

A mixture of 40 g of pulverized arsenic and 8 g of silver powder was heated to 400°, and a stream of hydrogen passed through for 3 hr. Then the temperature was increased to 520° and the vapour of chlorobenzene (carried by nitrogen) was introduced at a rate of 8·3 cm³ of C_6H_5Cl per hour. A clear, yellowish liquid was the reaction product. Overnight the liquid blackened and metallic arsenic was precipitated.

Fractional distillation of the product from an input of 950 cm³ of C_6H_5Cl gave 2·5 g of yellowish liquid, b.p. 160°–170°/10 mm, which contained no arsenic. (Found: C, 65·28; H, 4·42; Cl, 30·85%). The composition of this compound is therefore nearly the same as that of C_6H_5Cl (Calc. C, 64·02; H, 4·48; Cl, 31·5%), but the boiling point is much higher than that of C_6H_5Cl. It probably consists of chlorinated polynuclear aromatics.

Copper- and zinc-catalysed reaction of bromobenzene with arsenic

A mixture of 50 g of pulverized arsenic, 10 g of copper powder, and 5 g of zinc dust, supported on asbestos, was heated to 400° and a stream of hydrogen was passed through for 3 hr. Then the temperature was increased to 500° and bromobenzene was introduced at a rate of 14·5 g/hr. A clear yellowish liquid was the reaction product.

Fractional distillation of the material from an input of 750 g of C_6H_5Br gave:

(1) b.p. 75–79°/760 mm, 60 g of C_6H_6, or 8·7 per cent;
(2) b.p. 149–156°/760 mm, 596 g of C_6H_5Br recovered, or 86·3 per cent;
(3) b.p. 95–116°/10 mm, 32 g of $C_6H_5AsBr_2$ + $AsBr_3$ or 4·6 per cent;
(4) b.p. 58–95°/0·05 mm, 3 g of unidentified product or 0·4 per cent.

A careful re-fractionation of Fraction 3 yielded pure $C_6H_5AsBr_2$ (7·5 g or 1·1 per cent). (Found: C, 22·74; H, 1·47; Br, 51·33. Calc. C, 23·10; H, 1·62; Br, 51·25%); By using silver as a catalyst the yield of $C_6H_5AsBr_2$ under the same conditions was 10 per cent instead of 1·1 per cent.

The same reaction was repeated at 600° and with a furnace where the heating zone was 60 cm long instead of 30 cm. The tube was charged with a mixture of 100 g of As, 20 g of Cu and 10 g of Zn supported on 40 g of asbestos. Bromobenzene was introduced at a rate of 22·5 g/hr. From an input of 225 g of C_6H_5Br, 233 g of crude products were obtained. Fractional distillation yielded:

(1) b.p. 51–78°/760 mm, 69 g of C_6H_6 or 30·7 per cent;
(2) b.p. 38–110°/111 mm, 102 g of C_6H_5Br or 44·6 per cent;
(3) b.p. 95–116°/11 mm, 50 g of $C_6H_5AsBr_2$ + $AsBr_3$ or 22·3 per cent;
(4) b.p. to 150°/11 mm, 5 g of unidentified product or 2·4 per cent.

Copper- and zinc-catalysed reaction of vinyl bromide with arsenic

The reaction of $CH_2{=}CHBr$ with a contact mass exactly the same as that above, but at 460°, gave 100 g of liquid products in 29 hr. Fractional distillation yielded (besides HBr and unreacted vinyl bromide):

(1) b.p. 24–60°/20 mm, 3·8 g of fore-run or 8·4 per cent;
(2) b.p. 60–64°/20 mm, 6 g of $(CH_2{=}CH)AsBr_2$* or 12·8 per cent;

* Reported boiling point in the literature.

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(3) b.p. 73–76°/14 mm, 22 g of $(CH_2{=}CH)AsBr_2$ or 46·8 per cent;
(4) b.p. 85–99°/14 mm, 15 g of $AsBr_3$ or 32 per cent.

The same reaction carried out at 350° produced nothing but a mirror of arsenic just beyond the heating zone. At 500° a much better yield per hour was obtained, but by far the greater part of the reaction product was $AsBr_3$.

A similar experiment in which the proportion of zinc in the contact mass was doubled gave
(1) b.p. 60–64°/20 mm, 4·8 g of $(CH_2{=}CH)_2AsBr$ or 3·3 per cent;
(2) b.p. 73–76°/14 mm, 34·5 g of $CH_2{=}CHAsBr_2$ or 23·2 per cent;
(3) b.p. 85–93°/14 mm, 109·5 g of $AsBr_3$ or 73·5 per cent.

Copper- and zinc-catalysed reaction of vinyl chloride with arsenic

A mixture of 50 g of arsenic, 10 g of copper and 5 g of zinc supported on 30 g of asbestos was heated to 400° in an atmosphere of H_2 for 3 hr, and then $CH_2{=}CHCl$ was introduced. Over an interval of 35·5 hr, 34 g of liquid product was obtained. After the first distillation (b.p. 100–130°), 22 g of product was obtained, which separated on standing at room temperature into two layers. The upper layer consisted of $(CH_2{=}CH)_2AsCl$, b.p. 105–106°, 6 g (= 26·2 per cent); the lower layer (16 g) was composed of what appeared to be $CH_2{=}CHAsCl_2$ and $AsCl_3$, which could not be separated by distillation.

Copper (II) *chloride catalysed reaction of methyl chloride with antimony*

A mixture of 40 g of pulverized antimony and 10 g of copper (II) chloride was heated to 450° for 5 hr in a stream of hydrogen. In the first 3 hr $SbCl_3$ was formed. The temperature was dropped to 372° and the hydrogen was replaced by methyl chloride, introduced at a rate of 5 cm³/min at room temperature. Over an interval of 170 hr liquid products collected at a rate of 0·14 g/hr, which then declined to 0·04 g/hr. The reaction product was fractionally distilled. It was not possible to obtain a colourless liquid because after a short time the distillate always turned black. For this reason the remaining undistilled product was butylated with $n\text{-}C_4H_9MgBr$, hydrolysed with a solution of ammonium chloride, and then fractionally distilled. The fractions were:

(1) $(CH_3)_2SbC_4H_9$, b.p. 37–65°/15 mm. (This product contained hydrocarbons (by-product from Grignard) which could not be separated from $(CH_3)_2SbC_4H_9$ by means of distillation, so the chief product was isolated from this fraction as the CH_3I adduct, $(CH_3)_3C_4H_9SbI$, prepared by adding excess CH_3I at room temperature). (Found: C, 23·78; H, 5·25; I, 36·39. Calc. C, 23·96; H, 5·17; I, 36·17%). The yield was 3·55 g corresponding to 1·89 g of $(CH_3)_2SbCl$ (9·70 per cent). (2) $CH_3Sb(C_4H_9)_2$, b.p. 84–86°/9 mm. (Found: C, 42·97; H, 8·18. Calc. C, 43·06; H, 8·43%).

(2) The yield was 13·75 g, corresponding to 11·37 g of CH_3SbCl_2 (58·21 per cent).

(3) $(C_4H_9)_3Sb$, b.p. 118°/9 mm. (Found: C, 47·01; H, 9·25. Calc. C, 49·17; H, 9·29%). The yield was 8·05 g, corresponding to 6·27 g of $SbCl_3$ (32·08 per cent).

Copper-catalysed reaction of methyl bromide with antimony

A mixture of 100 g of pulverized antimony and 10 g of copper powder (on asbestos) was heated to 350° in an atmosphere of hydrogen for 3 hr, and then CH_3Br was introduced. Over an interval of 32 hr, 181 g of liquid product was obtained. From the first distillation 149 g of liquid products were obtained, which yielded on fractionation:

(1) b.p. 74–82°/14 mm, 57 g of $(CH_3)_2SbBr$ (= 38 per cent), m.p. 85° (lit. 89°). (Found: Br, 34·34; C, 11.13; H, 2·35. Calc. Br, 34·49; C, 10·36; H, 2·61%).

(2) b.p. 120–130°/14 mm, 60 g of CH_3SbBr_2 (= 40 per cent), m.p. 42° (lil. 42°). (Found: Br, 51·81%). Calc. Br, 53·88%).

(3) b.p. 136°/2 mm, 32 g of $SbBr_3$ (= 22%), m.p. 93° (lit. 96·6°). (Found: Br, 64·15. Calc. Br, 66·32%).

Copper-catalysed reaction of bismuth with methyl chloride

Forty grammes of pulverized bismuth and 8 g of copper powder were mixed and heated to 350° in an atmosphere of hydrogen for 3 hr. Then methyl chloride was introduced at a rate of 5 cm³/min. The temperature was varied over the range of 220°–350°, but in no case could any methyl bismuth

chloride be collected. The only reaction product was a metallic mirror of bismuth just beyond the heating zone.

Copper-catalysed reaction of methyl bromide with bismuth

A similar experiment with CH_3Br gave no product at 350° or 300°, but at 250° a yellow crystalline solid was formed just beyond the heating zone. Over an interval of 16 hr 2 g of the yellow crystals were isolated. (Found: Br, 42·06; C, 3·17; H, 1·26. Calc. for CH_3BiBr_2: Br, 41·64; C, 3·13; H, 0·78%).

DISCUSSION

This survey indicates that the reaction of hydrocarbon halides with Group V elements proceeds in much the same way as that with the elements of Group IV, and at temperatures which correspond quite closely. Just as the reaction of lower alkyl and aryl halides with silicon is a rather general reaction, but becomes less generally applicable to germanium[7] and almost specific for methyl chloride with tin,[3] so the reaction is found here to be more general for arsenic than for antimony or bismuth. It appears that the reaction is applied most successfully to the synthesis of the methyl chloro- and bromoarsines, the vinyl bromoarsines, and the methyl bromostibines. In general, the hydrocarbon bromides give better yields than do the corresponding chlorides.

It may also be concluded that CH_3Br is partially pyrolysed at the reaction temperatures and the HBr so formed may react to form $AsBr_3$, especially if the recovered bromide is recycled. At the reaction temperature, the tribromide converts $(CH_3)_2AsBr$ to CH_3AsBr_2,[6] as can be shown by the deliberate addition of HBr to the methyl bromide (See Expt. 12, Table 1). The production of HBr by pyrolysis is less when glass wool is used as a support for the metal than when asbestos is used, and so the yield of methyl bromoarsines is better.

Vinyl bromide reacts poorly with arsenic when copper alone is used as a catalyst, but reacts better when copper and zinc are used jointly. Bromobenzene reacts better with arsenic when silver is used as a catalyst, but copper plus zinc may be used instead. Antimony reacts poorly with CH_3Cl, but reasonably well with CH_3Br. Any organobismuth halides formed in the direct reaction of bismuth are principally decomposed at the reaction temperature. The related reactions of phosphorus constitute a special case which is being studied separately.[8]

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[7] E. G. ROCHOW, R. DIDTSCHENKO and R. C. WEST, *J. Amer. Chem. Soc.* **73**, 5486 (1951); E. G. ROCHOW, *Ibid.* **72**, 198 (1950).
[8] L. MAIER, *Angew. Chem.* **71**, No. 18, 574, 575 (1959).

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METALLIC COMPLEXES OF DIMETHYLSULPHOXIDE

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Abstract—Stable crystalline complex compounds of dimethylsulphoxide (DMSO) with metallic perchlorates and/or halides have been prepared and partially characterized by their melting points and infra-red spectra in the 2–15 μ region. Evidence from the spectra suggests that coordination through the oxygen is occurring for all metals studied with the likely exception of Pd(II). Most striking about the compounds is that relatively stable anhydrous complexes were obtained from hydrated salts, suggesting a possible route to the preparation of anhydrous salts. With the divalent metals and Fe(III) the empirical formulas for the complexes of the halides show one, two, or three moles of DMSO per mole of salt, suggesting that halogen is also coordinated in all cases. The aluminium chloride complex with six DMSO molecules is an exception. With the perchlorate salts the empirical formulas indicate maximum normal coordination by DMSO in all cases except $Pb(ClO_4)_2 \cdot 3DMSO$, in which three-co-ordination appears likely. If the decrease in the strength of the S—O bond is taken as a measure of the increase in the oxygen–metal bond strength, the following series of divalent ions arises:

$$Zn < Hg < Ni < Mn < Co < Cd < Fe < Pb < Cu.$$

RECENTLY the compound dimethylsulphoxide (DMSO) has become generally available and its solvent action toward inorganic complexes appears to be very promising. A survey of the literature on DMSO and on sulphoxides in general failed to reveal any studies on the donor characteristics of these compounds. It was therefore of interest to undertake such studies particularly since the possibility does exist for coordination by the $R_2S{=}O$ molecule to a metal ion through either the sulphur or the oxygen atom.

That sulphoxides can act as donor molecules is suggested by some early work of HOFMANN and OTT[1]. They reported in 1907 that from a reaction mixture consisting of toluene, thionyl chloride and ferric chloride, a crystalline product could be isolated which they formulated as $(CH_3C_6H_4)_2SO, FeCl_3$. Upon treatment of this compound with warm water they obtained tolylsulphoxide. Similar compounds were reported to form from benzylsulphoxide and phenylsulphoxide. ADDISON and SHELDON[2] reported more recently that when N_2O_4 was used to oxidize alkyl sulphides to sulphoxides, addition compounds of the N_2O_4 with the latter could be isolated. For example, with DMSO the 1 : 1 compound $DMSO \cdot N_2O_4$ was obtained and the authors believed that the sulphur is the donor atom. That the oxygen in sulphoxides forms hydrogen bonds has been suggested by BARNARD *et al.*[3], who reported that the characteristic S—O bond stretching frequencies of sulphones and sulphoxides are lowered by hydrogen bonding in the solvents CH_3OH or $CHCl_3$.

In a very recent study of the general behaviour of metal tetrafluorides toward a variety of organic donor molecules, MUETTERTIES[4] reports the preparation of the following complexes of DMSO : $MF_4 \cdot 2DMSO$, where M = Ti, Zr, Si, Ge, Sn, Mo.

[1] K. A. HOFMANN and K. OTT, *Ber. Dtsch. Chem. Ges.* **40**, 4930 (1907).
[2] C. C. ADDISON and J. C. SHELDON, *J. Chem. Soc.* 2705 (1956).
[3] D. BARNARD, J. M. FABIAN and H. P. KOCH, *J. Chem. Soc.* 2442 (1949).
[4] E. L. MUETTERTIES, *J. Amer. Chem. Soc.* **82**, 1082 (1960).

We report the preparation and partial characterization of crystalline DMSO complexes of twenty-two metallic salts representing twelve different metals. The new compounds, perchlorates and halides, with their respective stoicheiometries, colours and melting points are listed in Table 1 along with the position of the perturbed S=O and C—S stretching frequencies.

TABLE 1.—DMSO COMPLEXES, COLOURS, MELTING POINTS AND INFRA-RED S=O AND C—S FREQUENCIES IN cm^{-1}

Compound	Colour	m.p. (°C)	S=O band max.*	C—S band max.*
DMSO	—	—	1053	697
$Zn(ClO_4)_2 \cdot 4DMSO$	white	73–74	1018	717
$AlCl_3 \cdot 6DMSO$	white	—	(1009)	(727)
$HgCl_2 \cdot DMSO$	white	125–126	1005(1030)	711(709)
$NiCl_2 \cdot 3DMSO$	blue	67	1004(999)	716(714)
$Ni(ClO_4)_2 \cdot 6DMSO$	light green	explodes	1002	716
$Mn(ClO_4)_2 \cdot 6DMSO$	white	210·5–212	1001	716
$Co(ClO_4)_2 \cdot 6DMSO$	pink	242–244	1000	717
$CoCl_2 \cdot 3DMSO$	blue	97–99	999(1000)	717(713)
$CdBr_2 \cdot DMSO$	white	173	(996)	(709)
$Ga(ClO_4)_3 \cdot 6DMSO$	white	explodes	993	727
$CdCl_2 \cdot DMSO$	white	decomposes	991	716
$Fe(ClO_4)_3 \cdot 6DMSO$	light yellow	explodes	989	723
$CuBr_2 \cdot 2DMSO$	orange	dec. 115	(989)	(724)
$Fe(ClO_4)_2 \cdot 6DMSO$	yellow green	explodes	988	723
$FeCl_2 \cdot 2DMSO$	yellow	106–108	988(981)	722(720)
$PbCl_2 \cdot DMSO$	white	—	987	724
$CuCl_2 \cdot DMSO$	orange	dec. 125	(987)	(726)
$Pb(ClO_4)_2 \cdot 3DMSO$	white	124–127	986	710
$Cu(ClO_4)_2 \cdot 4DMSO$	aqua	explodes	986	722
$CuCl_2 \cdot 2DMSO$	light green	153–155	980(987)	728(726)
$PbBr_2 \cdot DMSO$	white	—	978	714
$PdCl_2 \cdot 2DMSO$	yellow	202–203·5	1118	732
$PtCl_2 \cdot \chi DMSO$	impure	—	~1110 (1030–1040)	737(724)

* Values in parentheses were obtained in KBr pellets, others from Nujol mulls.

EXPERIMENTAL

A. *Preparation of compounds*

All chemicals were of at least reagent grade quality and except for the DMSO, which was vacuum distilled, they were used without further purification.

$Co(ClO_4)_2 \cdot 6DMSO$, $Zn(ClO_4)_2 \cdot 4DMSO$. The appropriate hydrated salt was dissolved in a minimum amount of acetone and a slight excess of DMSO added. On cooling, crystals were obtained which were recrystallized from acetone. (Found: ClO_4, 27·3; Co, 7·97. Calc. for $Co(ClO_4)_2 \cdot 6C_2H_6SO$: ClO_4, 27·38; Co, 8·13. Found: ClO_4, 34·70; Zn, 11·0 Calc. for $Zn(ClO_4)_2 \cdot 4C_2H_6SO$: ClO_4, 34·55; Zn, 11·3).

$Fe(ClO_4)_3 \cdot 6DMSO$, $Ga(ClO_4)_3 \cdot 6DMSO$. The hydrated salt was dissolved in acetone and DMSO added. The solid complex precipitates immediately and is quite insoluble in acetone. The complex was purified by washing it thoroughly several times with hot acetone which removed any excess salt or DMSO. (Found: ClO_4, 36·0. Calc. for $Fe(ClO_4)_3 \cdot 6C_2H_6SO$: ClO_4, 36·38. Found: ClO_4, 35·4. Calc. for $Ga(ClO_4)_3 \cdot 6C_2H_6SO$: ClO_4, 35·8%).

$Mn(ClO_4)_2 \cdot 6DMSO$. The hydrated salt was dissolved in acetone and DMSO added. Better

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crystals were obtained if the salt was present in slight excess instead of the DMSO as in other cases. The complex was recrystallized from acetone containing a small amount of ether to reduce its solubility. (Found: ClO_4, 27·3. Calc. for $Mn(ClO_4)_2 \cdot 6C_2H_6SO$: ClO_4, 27·6%).

$Cu(ClO_4)_2 \cdot 4DMSO$, $Ni(ClO_4)_2 \cdot 6DMSO$. The hydrated salt was dissolved in ethanol, an equal volume of ether added and then DMSO. Crystals were obtained immediately or upon cooling in ice. Both complexes were recrystallized from acetone. (Found: ClO_4, 34·2; Cu, 10·4. Calc. for $Cu(ClO_4)_2 \cdot 4C_2H_6SO$: ClO_4, 34·62; Cu, 11·05. Found: ClO_4, 27·5; Ni, 8·15. Calc. for $Ni(ClO_4)_2 \cdot 6C_2H_6SO$: ClO_4, 27·4; Ni, 8·32%).

$Pb(ClO_4)_2 \cdot 3DMSO$. The hydrated salt was dissolved in ethanol, an equal volume of ether added, then DMSO. A slight excess of the salt was used. The complex apparently solvates readily so an excess of DMSO is undesirable. The product was recrystallized from acetone. (Found: ClO_4, 31·0; Pb, 31·8. Calc. for $Pb(ClO_4)_2 \cdot 6C_2H_6SO$: ClO_4, 30·86; Pb, 32·1%).

$Fe(ClO_4)_2 \cdot 6DMSO$. The hydrated salt was dissolved in acteone and DMSO added. The solution clouded at once and upon cooling light-green crystals were deposited. On heating the product in acetone a yellow solid was left undissolved, presumably some iron(III) compound, and the solution yielded very light green crystals upon cooling. The product decomposes slowly on standing, even in the absence of light, moisture and oxygen. (Found: ClO_4, 30·5. Calc. for $Fe(ClO_4)_2 \cdot 6C_2H_6SO$: ClO_4, 27·5).

$CoCl_2 \cdot 3DMSO$. (a) The hexahydrated salt was dissolved in acetone and a slight excess of DMSO added. On cooling crystals were obtained which were recrystallized from acetone. (b). The hydrated salt was dissolved in hot DMSO and cooling produced blue crystals. (Found: Cl, 19·2; Co, 15·9; DMSO, 64·2; C, 19·81; H, 5·34. Calc. for $CoCl_2 \cdot 3C_2H_6SO$: Cl, 19·5; Co, 16·2; DMSO, 64·3; C, 19·78; H, 4·98%).

$NiCl_2 \cdot 3DMSO$. The hydrated salt was heated in air (over a flame) until a uniform yellow-coloured product was obtained. This "dried" $NiCl_2$ was added to pure DMSO. The solution underwent the following color changes: yellow to green to blue. The DMSO solution was warmed to boiling and the undissolved $NiCl_2$ was removed by filtration. Cooling of the filtrate resulted in formation of blue crystals of the complex. Care was necessary to prevent exposure of the compound to the atmosphere because of its strong hydroscopic tendencies. The product was washed with benzene and dried *in vacuo*. (Found: Cl, 18·0; DMSO, 63·6; C, 18·73; H, 5·30. Calc. for $NiCl_2 \cdot 3C_2H_6SO$: Cl, 19·5; DMSO, 64·5; C, 19·80; H, 4·90%).

$CuCl_2 \cdot 2DMSO$. (a) Anhydrous $CuCl_2$ was dissolved in DMSO with the evolution of heat; crystals were obtained upon cooling, filtered and washed with ether. (b) DMSO was added to a saturated solution of anhydrous $CuCl_2$ in absolute ethanol, a green solution resulting. A small volume of water was added to this solution and then ether, which caused crystallization of the green product. The crystals were washed with ether after filtration. (Found: Cu, 21·84; Cl, 24·3; DMSO, 53·3; C, 16·42; H, 4·39. Calc. for $CuCl_2 \cdot 2C_2H_6SO$: Cu, 21·85; Cl, 24·4; DMSO, 53·7; C, 16·52; H, 4·16%).

$CuCl_2 \cdot DMSO$. DMSO was added to a saturated solution of anhydrous $CuCl_2$ in absolute ethanol, producing a green solution. Addition of ether resulted in the formation of a bright orange crystalline solid. The product was isolated by filtration in a dry atmosphere. The orange complex is very hygroscopic. (Found: Cu, 29·5; Cl, 33·6; DMSO, 37·2; C, 11·90; H, 3·16. Calc. for $CuCl_2 \cdot C_2H_6SO$: Cu, 29·9; Cl, 33·4; DMSO, 36·7; C, 11·30; H, 2·85%).

$CuBr_2 \cdot 2DMSO$. Addition of DMSO to anhydrous $CuBr_2$ dissolved in absolute ethanol yielded orange crystals of the complex. These were collected by filtration and washed with absolute ethanol. (Found: Cu, 16·7, Br, 43·5; DMSO, 38·2. Calc. for $CuBr_2 \cdot 2C_2H_6SO$: Cu, 16·7; Br, 42·2; DMSO, 41·2%). (This DMSO analysis included a correction for oxidation of Br^- to Br_2 as well as oxidation of DMSO. See analytical procedures below.)

$HgCl_2 \cdot DMSO$. (a) $HgCl_2$ was dissolved in DMSO at about 60°C; cooling produced white crystals which were recrystallized twice from acetone. (b) A saturated etheral solution of $HgCl_2$ was treated with DMSO, white crystals forming immediately. These were washed with ether and air-dried. (Found: Cl, 19·9, 20·9; DMSO, 21·2. Calc. for $HgCl_2 \cdot C_2H_6SO$: Cl, 20·3; DMSO, 22·3%).

$FeCl_3 \cdot 2DMSO$. (a) Anhydrous $FeCl_3$ was dissolved in ether and some solid filtered off. DMSO was then added; the oil obtained could not be solidified by ether or benzene. The oil was placed in a vacuum for 10 hr, whereupon a yellow solid was obtained which, after crushing, was easily

recrystallized from acetone, washed with ether and vacuum-dried. (b) The hexahydrated chloride was dissolved in hot DMSO. Cooling the solution yielded yellow crystals of the complex. Recrystallization was effected from ethanol. No water bands were observed in the infra-red spectrum. (Found: Cl, 35·5; DMSO, 46·7; C, 14·57; H, 3·77. Calc. for $FeCl_3 \cdot 2C_2H_6SO$: Cl, 35·5; DMSO, 49·1; C, 15·05; H, 3·80%).

$AlCl_3$·6DMSO. Anhydrous $AlCl_3$ dissolved in ether solution was treated dropwise with DMSO. The white complex precipitated immediately and was washed with ether. It is very hygroscopic. (Found: Cl, 17·7; DMSO, 75·1. Calc. for $AlCl_3 \cdot 6C_2H_6SO$: Cl, 17·7; DMSO, 77·8%).

$PdCl_2$·2DMSO. Palladium chloride was dissolved in DMSO at an elevated temperature, the excess being filtered off if necessary, and upon cooling yellow crystals were obtained which are insoluble in acetone, ether and ethanol. Purification was accomplished by refluxing the solid in a 3:1 acetone–ethanol mixture. (Found: 31·75. Calc. for $PdCl_2 \cdot 2C_2H_6SO$: Pd, 31·90%).

$CdCl_2$·DMSO. The dihydrate was dissolved in hot DMSO and the solution cooled. Addition of ether promoted crystallization. The white product was filtered and washed with ether. (Found: Cl, 27·4, 26·8; DMSO, 29·8. Calc. for $CdCl_2 \cdot C_2H_6SO$: Cl, 27·2; DMSO, 29·9%).

$CdBr_2$·DMSO. An ethereal solution of $CdBr_2$ was treated with DMSO. White crystals of the complex formed immediately and were filtered and washed with ether. (Found: Br, 44·8, 45·4; C, 6·98; H, 2·01. Calc. for $CdBr_2 \cdot C_2H_6SO$: Br, 45·7; C, 6·86; H, 1·73%).

$PbCl_2$·DMSO, $PbBr_2$·DMSO. The lead halide was dissolved in DMSO at an elevated temperature and then the solution cooled until crystallization occurred. The filtered crystals were washed with hot acetone and dried in a vacuum. (Found: 19·4. Calc. for $PbCl_2 \cdot C_2H_6SO$: Cl, 19·9%). Found: 37·8. Calc. for $PbBr_2 \cdot C_2H_6SO$: Br, 38·6.

All compounds were stored in a vacuum desiccator to prevent their taking up moisture.

B. *Analytical procedures*

Perchlorate analyses were obtained by precipitation with nitron.[5] Halogen analyses were obtained by standard volumetric procedures using either $Hg(NO_3)_2$ or $AgNO_3$ as titrant. DMSO was analysed by dissolving the complex in water and following the procecure of DOUGLAS[6].

Metal analyses were obtained by specific gravimetric procedures found in standard texts. Carbon and hydrogen were determined by a commercial analytical laboratory.

C. *Infra-red spectra*

Infra-red spectra in the 2–15 μ region were obtained with a Perkin–Elmer Model 21 Recording Spectrophotometer employing NaCl optics. The pure DMSO was run as a film on a NaCl window. Most of the compounds were run as Nujol mulls since KBr pellets generally gave the poorer spectrum, presumably owing to partial decomposition of the complex under the conditions of pellet preparation.

DISCUSSION OF RESULTS

It appears that of the twenty-two different DMSO complexes prepared in this study there are no less than nine different stoicheiometric types of compounds. These are listed in Table 2 along with tentative suggested formulæ for the specific metals. The first three formulæ are based upon the reasonable assumption that the perchlorate ion will not co-ordinate to a metal ion, particularly if other ligands are present. The fourth formula, for the lead compound, is unusual in that it suggests three-co-ordination for the lead. The fifth formula, for the aluminium compound, seems reasonable since aluminium will always prefer to satisfy its co-ordination number with oxygen donors in preference to chloride ions. The formula for the ferric chloride compound is undoubtedly unusual and the suggested formula is pure speculation at this time. This compound, with the ones to be mentioned next warrant further investigation. The tentative formula suggestion for compound type number seven has some support from both the colour of the Co and Ni compounds and from their infra-red spectra.

[5] F. J. WELCHER, *Organic Analytical Reagents*. Van Nostrand, New York (1947).
[6] T. B. DOUGLAS, *J. Amer. Chem. Soc.* **68**, 1076 (1946).

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Both compounds have the deep blue colour characteristic of the tetrahedrally co-ordinated anion $[MCl_4]^{2-}$ (M = Co or Ni), rather than the weak pink or green colour of the hexaco-ordinated Co(II) or Ni(II). Formulation of the cation for each compound as $[M(DMSO)_6]^{2+}$ is strongly indicated by the near-identical infra-red spectra found for these halide complexes and the corresponding hexaco-ordinated perchlorate complexes discussed above (see Table 1). These compounds deserve further investigation; particularly valuable for verifying the suggested formulæ would be very accurate magnetic determinations and visible–ultra-violet spectral data.

TABLE 2.—STOICHEIOMETRIC TYPES OF COMPLEXES

Compound type		Tentative formula suggestion	Metal, M*
1.	$M(ClO_4)_2 \cdot 6DMSO$	$[M(DMSO)_6](ClO_4)_2$	Ga < Fe
2.	$M(ClO_4)_2 \cdot 6DMSO$	$[M(DMSO)_6](ClO_4)_2$	Ni < Mn < Co < Fe
3.	$M(ClO_4)_2 \cdot 4DMSO$	$[M(DMSO)_4](ClO_4)_2$	Zn < Cu
4.	$M(ClO_4)_2 \cdot 3DMSO$	$[Pb(DMSO)_3](ClO_4)_2$	Pb
5.	$MCl_3 \cdot 6DMSO$	$[Al(DMSO)_6]Cl_3$	Al
6.	$MCl_3 \cdot 2DMSO$	$[Fe(DMSO)_4Cl_2][FeCl_4]$	Fe
7.	$MCl_2 \cdot 3DMSO$	$[M(DMSO)_6[MCl_4]$	Ni < Co
8.	$MX_2 \cdot 2DMSO$	$[M(DMSO)_2X_2]$	Cu(X = Br) < Cu (X = Cl) < Pd (X = Cl)
9.	$MX_2 \cdot DMSO$	$[M(DMSO)X_2]$	Hg(X = Cl) < Cd (X = Br) < Cd(X = Cl) < Pb (X = Cl) < Cu(X = Cl) < Pb (X = Br)

* The order indicated is that of decreasing S–O frequency which has been tentatively assumed to be directly proportional to increasing oxygen–metal bond strength.

Since Cu(II) and Pd(II) are almost invariably four-co-ordinate the formulation given for number eight is reasonable. Conductivity data, not yet available, should verify this suggestion. Likewise three-co-ordination, suggested in number nine for Hg(II), Cd, Pb(II) and Cu(II), is not unlikely and might be similarly verified. However, the solid state co-ordination number may well be larger as for the well-known complexes,[7] $CuCl_3^-$, $CdCl_3^-$ and $HgCl_3^-$.

Perhaps the most striking feature of all of the complexes prepared is the lack of water of any kind in their formulations. None of the infra-red spectra contain bands due to water, co-ordinated or otherwise, yet almost all complexes were obtained using hydrated salts as starting materials. The careful removal of the DMSO from the anhydrous complexes may provide a general route to anhydrous salts. This is now under investigation.

The assignment of the very strong and broad 1053 cm^{-1} band in the spectra of pure liquid DMSO (run on a thin film sample) is made on the basis of the literature summary on sulphur–oxygen frequencies by BELLAMY[8]. Our spectral results with the metallic complexes of DMSO lend additional support to the assignment. The moderately strong band at 697 cm^{-1} is assigned to the C—S stretching vibration, again on the basis of BELLAMY's literature summary.[8] The shift in this band found for the metallic complexes supports this assignment also.

[7] H. BRASSEUR and L. PAULING, *J. Amer. Chem. Soc.* **60**, 2886 (1938).
[8] L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules* (2nd Ed.) pp. 350–366. John Wiley, New York (1958).

That the sulphur–oxygen bond in sulphoxides (and sulphones) has considerable double bond character has received both experimental[3,9] and theoretical[10] support. It is expected then that co-ordination through the oxygen of the sulphoxide to a metal ion will reduce the double bond character and shift the S=O stretching frequency to lower values. SHELDON and TYREE[11] studied the P—O band in the infra-red spectra of solid addition compounds between POX_3 (X = Cl, C_6H_5) compounds and metal halides and found a shift to lower frequencies with respect to the pure POX_3. They interpreted this shift as suggesting bonding through oxygen. Likewise the shift to lower frequencies (See Table 1) of the S—O band found in this study with all DMSO compounds except the Pd(II) one (and an impure Pt(II) one) strongly suggests coordination through the oxygen. The magnitude of the shift to lower frequencies varies from 35 to 75 cm^{-1} in the compounds reported. The shift to a higher frequency (by 100 cm^{-1}) in the case of the Pd(II) compound would seem to rule out co-ordination through oxygen and suggests that sulphur co-ordination is occurring.

If it is assumed that the decrease in the strength of the S—O bond corresponds to an increase in the strength of the oxygen–metal bond. The following stability series arise: (a) for divalent chlorides,

$$Hg < Ni < Co < Cd < Pb < Cu;$$ (b) for divalent perchlorates,

$$Ni < Mn < Co < Fe < Pb < Cu;$$ (c) for trivalent ions, $Al < Ga < Fe$.

The C—S band for all complexes studied is shifted to higher frequencies indicating a strengthening of this bond. The shifts range in magnitude from 12 to 35 cm^{-1}, the latter value being for the Pd(II) compound.

Analogous complexes are formed by diphenylsulphoxide (DPSO) and these are now being prepared and investigated. It is interesting that all of the metal ions reported here which form DMSO complexes have been found to form stable DPSO complexes except for Pd(II). The replacement of methyl groups with phenyl groups on the sulphur may hinder the expected sulphur co-ordination for this metal.

Note added in proof: F. A. COTTON and R. FRANCIS [*J. Amer. Chem. Soc.* **82**, 2986 (1960)] have recently reported the preparation and preliminary study of a large number (35) of metallic complexes of dimethylsulphoxide. They have characterized several of them by spectral and magnetic measurements and their results confirm our infra-red results which have indicated metal to sulphur bonding only in a palladium complex. It is of interest that many of the structures which we have suggested are substantiated by their more thorough study of the properties of these new complexes.

[9] G. M. PHILLIPS, J. S. HUNTER and L. E. SUTTON, *J. Chem. Soc.* 146 (1945).
[10] H. P. KOCH, *J. Chem. Soc.* 408 (1949); H. P. KOCH and W. MOFFITT, *Trans. Faraday Soc.* **47**, 7 (1951). W. MOFFITT, *Proc. Roy. Soc.* A **200**, 409 (1950).
[11] J. C. SHELDON and S. Y. TYREE, *J. Amer. Chem. Soc.* **80**, 4775 (1958).

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J. Inorg. Nucl. Chem., 1961, Vol. 16, pp. 225 to 232. Pergamon Press Ltd. Printed in Northern Ireland

DEUTEROFLUOBORIC ACID AND NITRON DEUTEROTETRAFLUOROBORATE

THE STRUCTURE OF NITRON SALTS

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Abstract—Deuterofluoboric acid was prepared from deuteroboric acid and deuterium fluoride or anhydrous silver tetrafluoroborate and deuterium chloride. It was analysed in the form of the insoluble nitron–DBF_4 salt. A structural investigation of the salt resulted in suggesting an aromatic triazolium tetrafluoroborate structure. Similar structures are proposed for other nitron salts used in inorganic analytical chemistry.

DEUTEROFLUOBORIC acid was required for experimental work. No description of the compound could be found in the literature, although in a previous paper we mentioned[1a] that anhydrous DF and BF_3 behave like DBF_4 in the presence of a nucleophilic deuteron acceptor and the system can be used as a deuterating agent for aromatic hydrocarbons.

In order to obtain deuterofluoboric acid in heavy water solution an analogy of the fluoboric acid preparation was carried out by use of deuteroboric acid and a solution of DF in heavy water

$$D_3BO_3 + 4DF \xrightarrow{D_2O} DBF_4 + 3D_2O$$

Deuteroboric acid was obtained by deuterolysis of BCl_3

$$2BCl_3 + 6D_2O \rightarrow 6DCl + 2D_3BO_3$$

Heavy water solutions of DF could be conveniently prepared by dissolving anhydrous silver fluoride in heavy water and reacting it with the equivalent amount of DCl or DBr.

A more suitable method of preparation was found in the reaction of anhydrous silver tetrafluoroborate (in heavy water or organic solution) with anhydrous DCl (or DBr)

$$AgBF_4 + DCl \rightarrow AgCl + DBF_4$$

Deuterofluoboric acid, similarly to fluoboric acid, is non-existent in the absence of deuteron acceptor solvents. It was found from BF_3 vapour pressure measurements that anhydrous DF and BF_3 did not form DBF_4 in the temperature range of +20 to −100°C.*

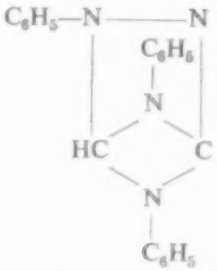
For its analytical determination deuterofluoboric acid can be titrated similarly to fluoboric acid or determined gravimetrically in the form of the stable, insoluble nitron–DBF_4 salt.

* Solubility and conductivity measurements of BF_3 in liquid, anhydrous DF point however to the equilibrium $BF_3 + 2DF \rightleftharpoons D_2F^+ + BF_4^-$, similarly to the one postulated by KILPATRICK[1b] for the anhydrous HF–BF_3 system. In anhydrous DF as solvent autodeuterolysis takes place $DF + DF \rightleftharpoons D_2F^+ + F^-$ (or DF_2^-) and boron trifluoride displaces the equilibrium to the right by the reaction $BF_3 + F \rightleftharpoons BF_4$.

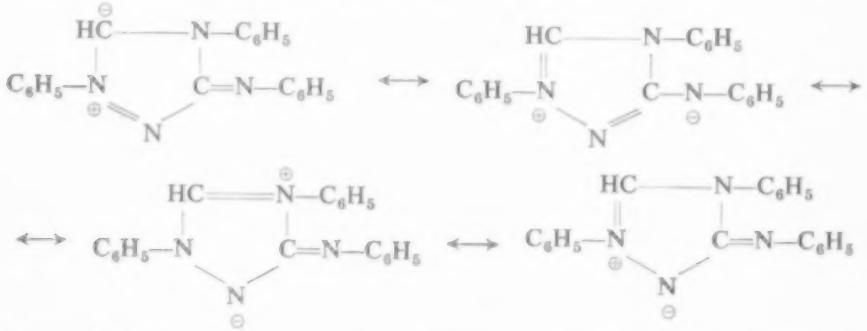
[1a] G. A. OLAH and S. J. KUHN, *J. Amer. Chem. Soc.* **80**, 6535 (1958); [b] M. KILPATRICK and F. E. LUBORSZKY, *J. Amer. Chem. Soc.* **76**, 5865 (1954).

The preparation of nitron–DBF_4 offered a possibility to investigate the structure of nitron salts. Nitron and related "endomethylene" compounds were first described by BUSCH[2]. The low solubility of nitron salts made nitron a useful reagent in inorganic analytical chemistry. The nitron method is used in the gravimetric determination of nitrates, perchlorates, tetrafluoroborates and perrhenates.

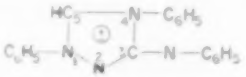
The endocyclic structure for nitron



proposed by BUSCH, was not acceptable because of stereochemical data[3] and results of investigation of its basic degradation products.[4] SCHONBERG[3] was the first to suggest a "Zwitter-ion" structure for nitron, which was later found to be in agreement with the observed high dipole moment of nitron.[5] Some of the possible contributing zwitter-ion structures for nitron may be formulated:



SIMPSON[6] introduced the term *meso-ionic* for molecules with a mesomeric structure derived from a number of ionic (in the sense of zwitterionic) forms. He also suggested the use of the symbol $\pm$.[7] Accordingly the structure of nitron as a *meso-ionic* compound can best be represented in the following way



Meso-ionic structure of nitron

[2] M. BUSCH, *Ber. Dtsch. Chem. Ges.* **38**, 859 (1905).
[3] A. SCHONBERG, *J. Chem. Soc.* 824 (1938).
[4] R. KUHN and H. KAINER, *Angew. Chem.* **65**, 442 (1953).
[5] F. L. WARREN, *J. Chem. Soc.* 1100 (1938).
[6] J. C. E. SIMPSON, *J. Chem. Soc.* 95 (1946).
[7] For a comprehensive treatment of the topic see W. BAKER and W. D. OLLIS, *Quart. Rev.* **11**, 15 (1957).

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All the atoms taking part in the hydbrid structure are shown as linked by single bonds only. The bright yellow colour of nitron however obviously points to a high degree of participation of the structures involving an exocyclic C=N bond possibly conjugated with the ring unsaturation.

Nitron–DBF_4 is colourless or slightly greyish white, similar to other nitron salts. It melts at 227–227·5° (uncorrected). It has a high stability against aqueous HCl and other aqueous acids even at 200°C (with obvious deuterium–hydrogen exchange

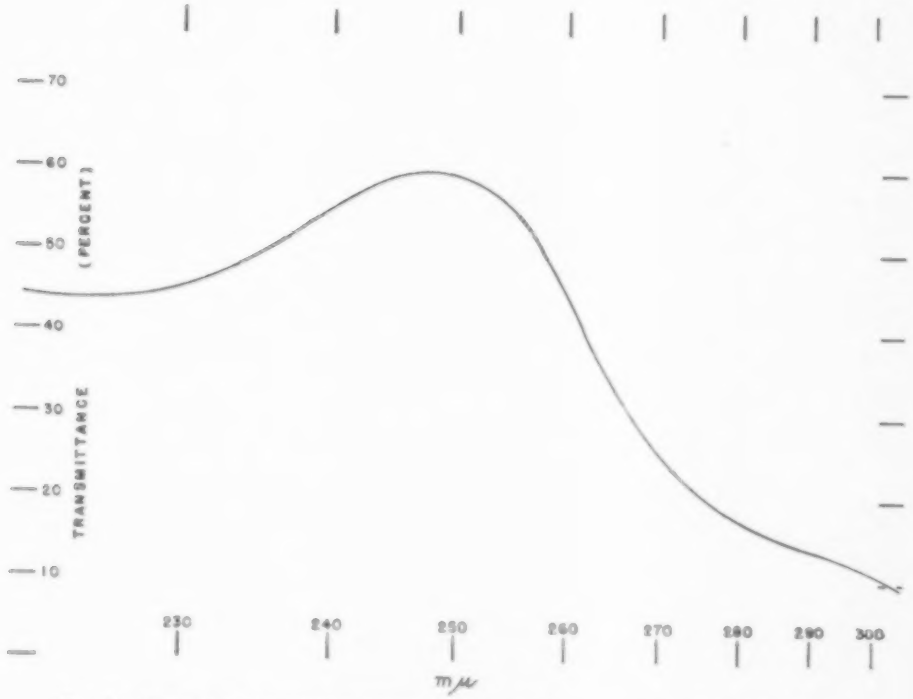
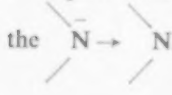


FIG. 1.—Ultra-violet absorption spectrum of nitron–DBF_4 concentration = $9{\cdot}0 \times 10^{-3}$ g/l. (in methanol)

taking place). Alcoholic potassium hydroxide, however, degradates it to triphenyl guanidin which can be dehydrogenated to benzolazo diphenyl formamidine (m.p. 104° no melting point depression and agreement of infra-red spectrum with synthetic sample in accordance with KUHNS data.[4])

The ultra-violet and infra-red absorption spectra of nitron–DBF_4 were taken. The ultra-violet absorption spectrum shows a strong absorption maximum at 248 mμ, characteristic of an aromatic type of structure. KUHN and KAINER[4] observed similar maxima for nitron–HCl and nitron–CH_3I in methanol, but found the absorption maxima for nitron itself (indioxane) at 270 and 295 mμ. Our findings show a strong absorption maximum at 250 mμ for nitron in methanol solution. The fact that



the N → NH transition in 5-amino tetrazol and tetrazol respectively and similarly

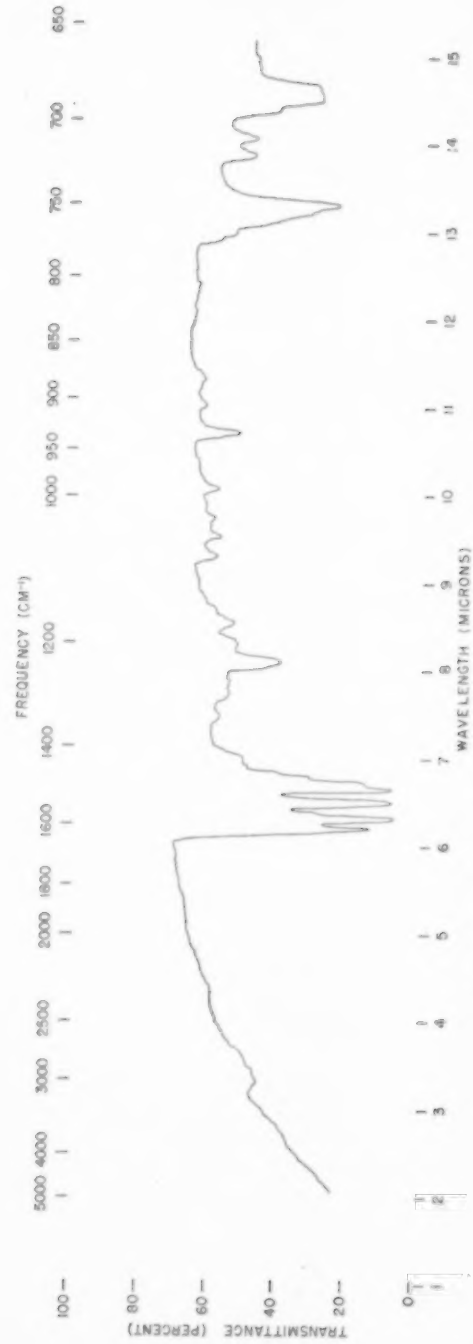


FIG. 2.—Infra-red absorption spectrum of nitron (Nujol-Fluorolube S30 mull).

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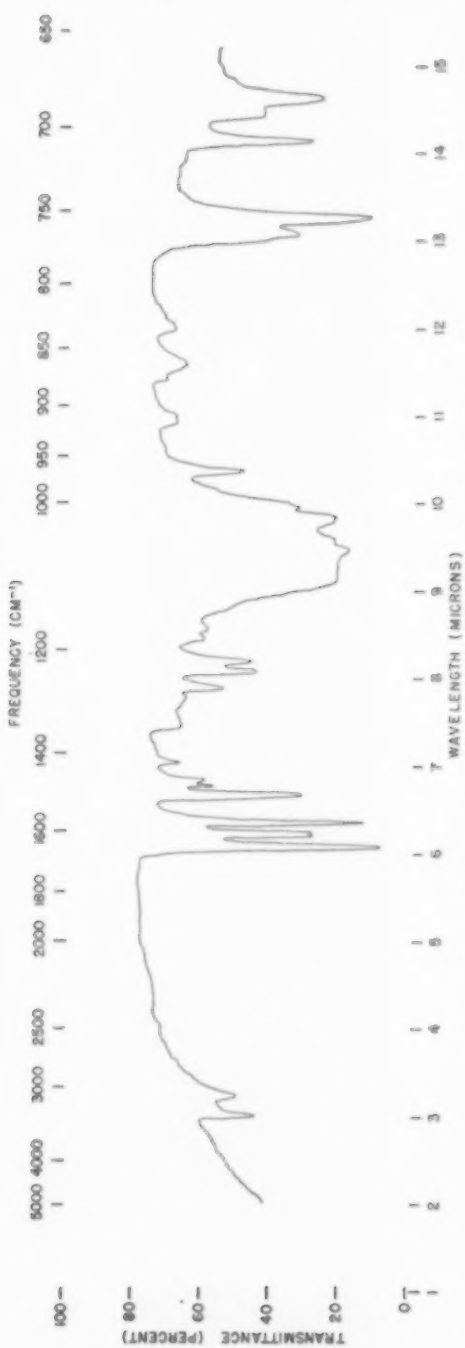

FIG. 3.—Infra-red absorption spectrum of nitron–HBF_4 (Nujol-Fluorolube S30 mull).

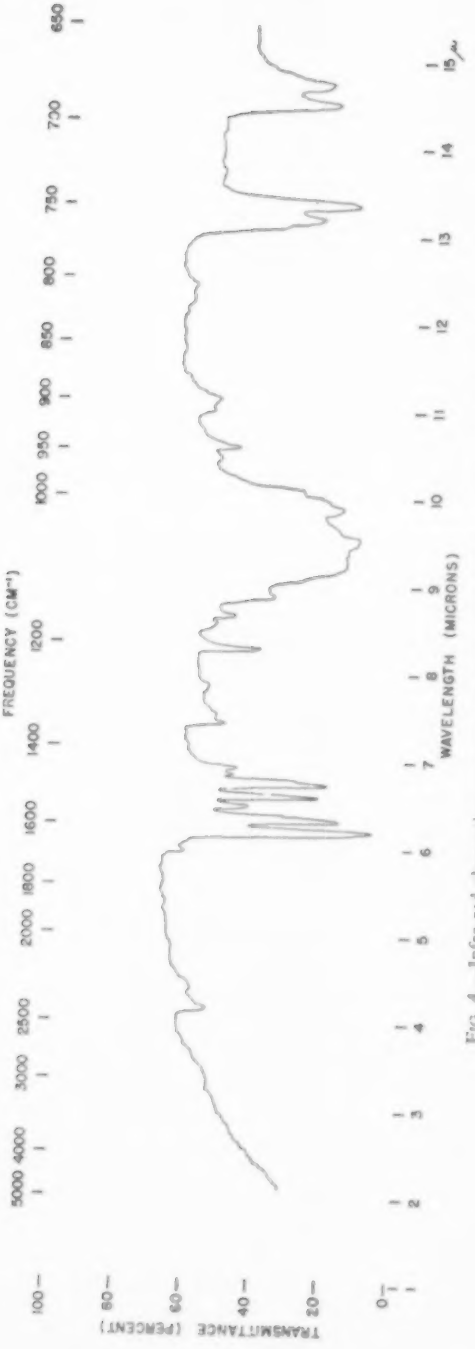

FIG. 4.—Infra-red absorption spectrum of nitron–DBF_4 (Nujol-Fluorolube S30 mull).

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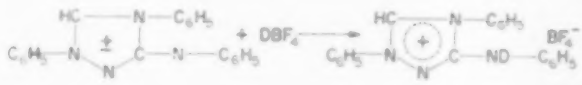
in C,N-diphenyl-N′-5-tetrazoyl-tetrazolium betain and triphenyl tetrazolium chloride[4] cause no remarkable shift of the absorption to the red, can explain this finding. Normal tetrazols[8] and triazols[9] show only end absorption over 210 mμ in the ultra-violet region, but their salts have maxima in the 250 mμ region.

The infra-red spectrum of nitron–DBF_4 was compared with that taken of nitron–HBF_4. A strong N—D stretching frequency at 2432 cm^{-1} and a C—D stretching frequency at 2287 cm^{-1} compared with the corresponding N—H stretching at 3300 cm^{-1} and C—H stretching at 3067 cm^{-1} in nitron–HBF_4. The relative intensities obviously point to predominant N-deuteration (presumably at the exocyclic nitrogen, but the infra-red spectrum alone can not differentiate sufficiently between this and the endocyclic N-deuteration) and some acid catalysed ring C-deuteration. The absorption peaks in the 1500–1650 cm^{-1} region are attributed to the ring bendings in the heterocyclic ring. The strong broad maximum at 1060 cm^{-1} is due to the BF_4^- anion.*

The high melting point, stability, resistance to acid hydrolysis, basic degradation products, absorption and NMR spectra of nitron deuterotetrafluoroborate ($C_{20}H_{16}N_4.DBF_4$) could best be explained by assuming a highly stable aromatic type triazolium structure. It is therefore suggested that nitron–DBF_4 is indeed 1,4-diphenyl-3-d-anilino-1,2,4-triazolium tetrafluoroborate (containing obviously a certain amount of ring deuterated C-5-d and possible ring N-d compounds) and the salt formation takes place in the following way.



Similarly other nitron salts should be interpreted as 1,2,4-triazolium salts. The triazolium cation possesses a highly stable aromatic structure and is closely related to the well known tetrazolium salts. A structure involving primarily ring nitrogen deuteration) in nitron salts and consequently an exocyclic C=N bond could be eliminated on the basis that this type of compounds should be easily hydrolysed by warming with aqueous HCl or other acids, a reaction not observed, even at 200° with nitron salts.

The structural problems connected with protonation and deuteration of meso ionic compounds with either stable, aromatic type cation formation or ring splitting and hydrolysis will be discussed from the organic point of view elsewhere. The author felt however that it was worthwhile to publish this part of his investigations in an inorganic journal, not only to report a new acid (deuterofluoboric acid) but also due to the fact that nitron, widely used as an inorganic analytical reagent is still

* *Note added in proof*: High resolution nuclear magnetic proton resonance (at 30,008 Mc, water as external reference) gave for nitron in dimethylformamide solution a single proton line at +146·2 cps (the DMF aldehyde proton is superposed on the phenyl protons and does not interfere in this region). Nitron–HBF_4 gave two proton lines at +144·8 and +167·5 cps. Nitron–DBF_4 had only one proton line at +145·2.

[8] J. H. Brydon, R. A. Henry, W. G. Finnegan, R. H. Boschan, W. S. McEwan and R. W. van Dolah, *J. Amer. Chem. Soc.* **75**, 4863 (1953).
R. A. Henry, W. G. Finnegan and E. Lieber *J. Amer. Chem. Soc.* **76**, 2894 (1954).
[9] L. W. Hantzel and F. R. Benson, *J. Amer. Chem. Soc.* **76**, 667 (1954).

unfortunately misrepresented in many text books[10] and publications as an "endocyclic" compound, with salts of unknown structure.

EXPERIMENTAL

The infra-red spectra were taken on a Perkin–Elmer Model 221 spectrophotometer using sodium chloride optics. The ultra-violet spectra were obtained on a Beckman Model DK2 spectrophotometer using 10 mm quartz cells.

Deuterofluoboric acid from D_3BO_3 *and* DF

Six and one half grammes (0·1 mole) of deuteroboric acid were added in small portions and with exclusion of moisture to 14·0 g of a 60 per cent solution of deuterium fluoride in heavy water (equivalent to 8·4 g = 0·4 mole of DF). The addition was carried out in a polyethylene flask, stirred with a Teflon coated magnetic stirrer and kept cold by immersion in iced-water. The temperature of the acid was not allowed to rise above 20°C. After the addition was completed the mixture was stirred for 30 min. A 45% DBF_4 solution in D_2O was obtained, as analysed in the form of nitron DBF_4.

Deuterofluoboric acid from anhydrous $AgBF_4$ *and* DCl

In 20 ml D_2O 19·6 (0·1 mole) anhydrous silver tetrafluoroborate was dissolved. To this solution was added, during vigorous stirring and exclusion of air moisture, a solution of 3·45 g (0·1 mole) DCl in 15 ml D_2O. Strong heat evolution was observed (cooling is needed if addition is too fast), and immediate precipitation of silver chloride. After the addition was completed the reaction mixture was shaken at room temperature for ½ hr. Thereafter the heavy water solution of the deuterofluoboric acid was filtered off from the silver chloride precipitate (in a filtering apparatus avoiding contact with air moisture). The silver chloride was washed twice with 2 ml portions of heavy water and the washings combined with the main product. A 18·5% DBF_4 solution in D_2O was obtained. More concentrated solutions were prepared by reacting heavy water solutions of anhydrous $AgBF_4$ with anhydrous DCl.

Nitron-DBF_4

In 10 ml dimethylformamide 6·24 g (0·02 mole) nitron was dissolved. 2·17 g (0·02 mole) DBF_4 was added as a heavy water solution. The solution remained homogenous, although deeper coloured. The solution was thereafter diluted with 80 ml D_2O. A light green coloured precipitate separated. After standing in a refrigerator for 2 hr, the precipitate was filtered (with exclusion of air moisture) washed with two 2 ml portions of D_2O and dried in a vacuum at 100°C over P_2O_5 for 5 hr. Yield 7·83 g nitron–DBF_4 (97·5%) m.p. 227–227·5°C (Found: N, 13·8; F, 18·6. Calc for $C_{20}H_{16}N_4DBF_4$ (mol. wt. 401·2) N, 13·4; F, 18·4%).

Acknowledgement—The author is indebted to Dr. D. COOK of this laboratory for obtaining the spectra and for help in their interpretation and to Dr. E. B. BAKER, Physical Research Laboratory, The Dow Chemical Co., Midland, Mich. for obtaining the NMR spectra.

[10] As examples: J. ROSIN, *Reagent Chemical and Standards* (3rd Ed.) p. 298. Van Nostrand, New York (1955); F. J. WELCHER, *Organic Analytical Reagents* Vol. 3, p. 138. Van Nostrand, New York (1947); W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT and J. I. HOFMANN, *Applied Inorganic Analysis* pp. 320, 788. John Wiley, New York (1953); A. I. VOGEL, *Quantitative Organic Analysis* (2nd Ed.) p. 123. Longmans, Green, London (1951).

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CHEMISTRY OF THE METAL CARBONYLS—IX

DIENE COMPLEXES OF IRON*

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Abstract—The complex 1,5-cyclo-octadiene–iron tricarbonyl is described. 1,4-Pentadiene and triiron dodecacarbonyl react to give 1,3-pentadiene–iron tricarbonyl. The nature of the product from 1,4-dihydromesitylene and iron carbonyls is discussed. Reaction between isoprene and iron carbonyls has been reinvestigated. The new compounds α-terpinene–iron tricarbonyl and alloöcimene–iron tricarbonyl are described. The preparation of a series of complexes $[CH_3CH{:}CHCH{:}CHR]Fe(CO)_3$ ($R = -CO_2C_2H_5$, $-CONH_2$, $-COCH_3$, $-CN$, $-CHO$) is reported.

THIS paper describes a number of diene complexes of iron obtained from reactions between iron carbonyls and various diolefins.

In 1930 REIHLEN *et al.*[1] reported studies on reactions between iron pentacarbonyl and the conjugated dienes butadiene, isoprene, and 2,3-dimethylbutadiene. A compound $C_4H_6{\cdot}Fe(CO)_3$ was obtained from butadiene, and compounds of composition $(C_5H_8)_2Fe(CO)_3$ and $(C_6H_{10})_2Fe(CO)_3$ were reported as formed from isoprene and dimethylbutadiene respectively. REIHLEN *et al.*[1] formulated the butadiene–iron compound as an adduct of butadiene in which the iron atom of an iron tricarbonyl group is σ-bonded to the 1,4-carbon atoms of butadiene. Recently, however, the compound was reinvestigated by HALLAM and PAUSON[2] who presented convincing evidence, based on ozonolysis, reduction, magnetic and spectral studies, that butadiene remains essentially intact in $C_4H_6{\cdot}Fe(CO)_3$. Because of this, a structure has been proposed[2] involving the hydrocarbon in a planar or nearly planar configuration, with the iron atom equidistant from the four carbon atoms of the C_4H_6 moiety. It was further suggested that the iron–carbon bonding in butadiene–iron tricarbonyl is more similar to that in ferrocene than to that in chelate complexes of non-conjugated diolefins. Attention was drawn to the fact that iron complexes of non-conjugated dienes had not been reported, suggesting that conjugation of the double bonds is very important if a stable diene complex of iron is to form. In view of these results it seemed worthwhile to investigate the reaction between an unambiguously unconjugated diene† and an iron carbonyl in order to

* Previous paper in this series, H. D. KAESZ, R. B. KING and F. G. A. STONE, *Z. Naturf.* In press. We are indebted to the Milton Fund and the Eugene Higgins Trust for financial support of this work.

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† The compound bicyclo-(2:2:1)-heptadiene–iron tricarbonyl has been reported by PETTIT[3] and by BURTON *et al.*[4] However, since bicyclo-(2:2:1)-heptadiene undergoes a Diels–Alder reaction with maleic anhydride, albeit only under very vigorous conditions[5], it is not clear whether the two double bonds of this hydrocarbon are acting independently in its metal complexes.

[1] O. REIHLEN, A. GRUHL, G. HESSLING and O. PFRENGLE, *Liebigs Ann.* **482**, 161 (1930).
[2] B. F. HALLAM and P. L. PAUSON, *J. Chem. Soc.* 642 (1958).
[3] R. PETTIT, *J. Amer. Chem. Soc.* **81**, 1266 (1959).
[4] R. BURTON, M. L. H. GREEN, E. W. ABEL and G. WILKINSON, *Chem. & Ind.* 1592 (1958).
[5] E. F. ULLMAN, *Chem. & Ind.* 1173 (1958).

determine whether conjugation in a diene is really essential for the existence of an iron tricarbonyl complex.

The recent isolation in this laboratory[6] of fairly stable 1,5-cyclo-octadiene derivatives of the Group VI metals [C_8H_{12}·$M(CO)_4$, M = Cr, Mo, W], prepared in order to extend the limits of the region in the Periodic Table containing transition metals which form olefin complexes, made it seem possible that 1,5-cyclo-octadiene(I) might also form a complex with iron. Although it proved impossible to form a compound C_8H_{12}·$Fe(CO)_3$ by heating together iron pentacarbonyl and 1,5-cyclo-octadiene,[7] reaction between triiron dodecacarbonyl and cyclo-octadiene in refluxing benzene afforded cyclo-octadiene–iron tricarbonyl as a volatile orange liquid, solidifying just below room temperature to a yellow solid. The cyclo-octadiene–iron complex,* also formed by irradiating a mixture of iron pentacarbonyl and 1,5-cyclo-octadiene, is very unstable, decomposing in a few hours at room temperature, even when kept under nitrogen. The thermal and oxidative instability of cyclo-octadiene–iron tricarbonyl, as opposed to butadiene–iron tricarbonyl, implies that conjugation in a diene leads to greater stability of the iron complex. However, besides differing in terms of conjugation and non-conjugation, 1,5-cyclo-octadiene and butadiene must have very different steric requirements. Consequently it seemed pertinent to study the reaction between triiron dodecacarbonyl and a 1,4-non-conjugated diene in which the two double bonds are separated by only one sp^3-hybridized carbon atom. 1,4-Pentadiene was chosen as the diene for this study. When this pentadiene was heated with triiron dodecacarbonyl in refluxing 2,2,4-trimethylpentane, a yellow, easily purified, volatile liquid of composition C_5H_8·$Fe(CO)_3$ was obtained. In contrast to C_8H_{12}·$Fe(CO)_3$, the pentadiene complex has a stability comparable with that of butadiene–iron tricarbonyl. It can be handled in air for several hours without oxidation, and remains undecomposed at room temperature for weeks under nitrogen. The stability of this complex led to the suspicion that 1,4-pentadiene had undergone rearrangement to 1,3-pentadiene in its reaction with triiron dodecacarbonyl at 100°, and that the C_5H_8·$Fe(CO)_3$ complex was in fact 1,3-pentadiene–iron tricarbonyl. This idea received further support from a study of the liquid film infra-red spectrum of the complex, which shows a band at 1380 cm^{-1} indicative of a CH deformation frequency in a C—CH_3 group, and from a study of the NMR spectrum of the complex which shows a prominent peak at 1·40 p.p.m. (low-field side of tetramethylsilane) in the region expected for methyl group protons. In order to confirm that the C_5H_8 moiety present in C_5H_8·$Fe(CO)_3$ was 1,3-pentadiene the complex was heated with triphenylphosphine to bring about displacement of the hydrocarbon ligand. This treatment afforded pure *trans*-1,3-pentadiene.

Formation of 1,3-pentadiene–iron tricarbonyl from 1,4-pentadiene, as well as the existence of duroquinone-iron tricarbonyl,[8] prompted an investigation of the reaction between triiron dodecacarbonyl and 1,4-dihydromesitylene(II) to determine whether 1,4-double bonds, connected by an sp^3 carbon atom lacking a π-orbital to effect conjugation between them, in a six-membered ring were suitably disposed to form

* After completion of this work we became aware through a personal communication that A. NAKAMURA and N. HAGIHARA, Osaka Univ., Japan, independently have prepared C_8H_{12}·$Fe(CO)_3$.

[6] T. A. MANUEL and F. G. A. STONE, *Chem. & Ind.* 1349 (1959); see also M. A. BENNETT and G. WILKINSON, *Ibid.* 1516 (1959); E. O. FISCHER and W. FRÖHLICH, *Ber.* **92**, 2995 (1959).
[7] T. A. MANUEL and F. G. A. STONE, *J. Amer. Chem. Soc.* **82**, 366 (1960).
[8] R. MARKBY, H. W. STERNBERG and I. WENDER, *J. Amer. Chem. Soc.* **80**, 1009 (1958).

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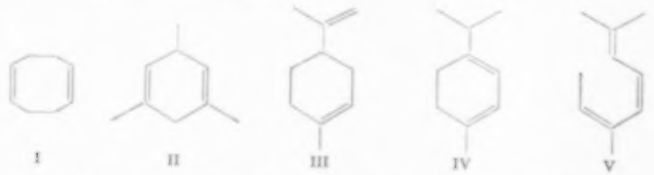
μ-bonds with iron. A complex $(CH_3)_3C_6H_5 \cdot Fe(CO)_3$ of the expected stoicheiometry was obtained, but its nuclear magnetic resonance spectrum was in agreement with its being 1,3-dihydromesitylene–iron tricarbonyl rather than 1,4-dihydromesitylene–iron tricarbonyl.

As mentioned earlier, previous workers[1] claimed that the reaction between isoprene and iron pentacarbonyl afforded a compound of composition $(C_5H_8)_2Fe(CO)_3$, rather than the expected isoprene–iron tricarbonyl. This curious result appeared worth reinvestigation, especially in view of the ready dimerisation of isoprene under certain conditions to the diolefin dipentene (d,l-limonenes)(III), found by other workers to form chelated olefin complexes with platinum.[9] However, in our hands, reaction between isoprene and iron



I II III IV V

pentacarbonyl yielded the expected isoprene–iron tricarbonyl. Pure limonenes* do not yield iron tricarbonyl derivatives, but a $C_{10}H_{16} \cdot Fe(CO)_3$ derivative is easily formed from the conjugated diene α-terpinene(IV). Some slight evidence for formation of this compound directly from isoprene and iron pentacarbonyl was obtained, but it could not be isolated. It is probable that the compound $(C_5H_8)_2Fe(CO)_3$ of REIHLEN *et al.*[1] was merely impure isoprene–iron tricarbonyl, contaminated by dipentene or other hydrocarbons produced from isoprene under the vigorous reaction conditions used. Indeed, to avoid side reactions isoprene–iron tricarbonyl is best prepared by irradiating a mixture of isoprene and iron pentacarbonyl with ultra-violet light or by reacting isoprene with triiron dodecacarbonyl in refluxing benzene.

During our work reactions were studied between iron carbonyls and 1,3-dienes possessing functional groups in conjugation with the diene system, in order to determine if iron would bond to any of the functional groups as well as to the diene system, thus giving an iron dicarbonyl complex. Ligands investigated were a series of butadienes which can be regarded as derivatives of 1,3-pentadiene, $CH_3CH{:}CHCH{:}CHR$($R = -CO_2C_2H_5$, $-CO_2H$, $-CN$, $-CONH_2$, $-COCH_3$, $-CHO$), and alloöcimene (2,6-dimethyl-2,4,6-octatriene)(V). With the exception of sorbic acid, the iron carbonyl derivatives obtained were volatile yellow to yellow-orange liquids or low-melting solids of composition $L \cdot Fe(CO)_3$, where L represents the ligand taken for reaction. Sorbic acid afforded a non-volatile brown material, soluble in organic solvents. The infra-red spectrum of this material, probably polymeric in nature, shows C—O stretching bands indicating the presence of an iron tricarbonyl group.

It is interesting that even though the various substituted 1,3-pentadienes have carbon–oxygen or carbon–nitrogen multiple bond systems conjugated with the diene

* Commercial limonenes react with iron carbonyls to afford a complex $C_{10}H_{16} \cdot Fe(CO)_3$. This compound was incorrectly thought to be dipentene–iron tricarbonyl[10] until degradation with triphenylphosphine was found to give α-terpinene, and chromatography of commercial limonenes established the presence of α-terpinene as well as, as previously noted[10] *p*-cymene.

[9] J. CHATT, L. M. VALLARINO and L. M. VENANZI, *J. Chem. Soc.* 2496 (1957).
[10] T. A. MANUEL and F. G. A. STONE, *Chem. & Ind.* 231 (1960).

system the resulting iron complex contains the $Fe(CO)_3$ group. Even alloöcimene, with three conjugated carbon–carbon double bonds, affords an iron tricarbonyl derivative. This was established by elemental analysis, analysis for CO groups, by the presence of an infra-red absorption band at 1653 cm^{-1} in the carbon–carbon double bond stretching region, and by treatment of alloöcimene–iron tricarbonyl with triphenylphosphine to give alloöcimene and *trans*-bis-(triphenylphosphine)iron tricarbonyl. Complexes of the type $L{\cdot}Fe(CO)_3$ where L is bound to iron by π-electrons are rare, examples being cycloheptatriene–, and thiophene–iron dicarbonyls.[4,11]*

EXPERIMENTAL

1. *Apparatus and preparation of reagents.* Infra-red spectra were recorded using a Perkin-Elmer Model 21 double-beam spectrophotometer with sodium chloride optics. Nuclear magnetic resonance spectra were recorded in carbon disulphide solution using hexamethyldisiloxane as an internal standard at 40 Mc/s by a Varian Model 4300B high-resolution spectrometer fitted with a super stabilizer.

Triiron dodecacarbonyl was prepared essentially by the same procedure as that described elsewhere[12] except that use of bromine was avoided, manganese dioxide being prepared by treating potassium permanganate with excess of 25 per cent ethanol. 1,4-Pentadiene taken for reaction was shown by gas chromatography to be better than 99 per cent pure. Ethyl sorbate was prepared by esterifying sorbic acid with absolute ethanol.[13] Sorbamide was prepared by treating sorboyl chloride with ammonia, and sorbyl methyl ketone prepared by base-catalyzed condensation of acetone with crotonaldehyde.[14] We are indebted to the Union Carbide Chemicals Corporation for a gift of sorbaldehyde (hexadienal). Sorbyl cyanide was prepared by the uncatalysed condensation of cyanoacetic acid with crotonaldehyde and decarboxylation of the cyanocarboxylic acid produced.[15] 1,4-Dihydromesitylene was prepared by the method described elsewhere.[16]

2. *1,5-Cyclo-octadiene–iron tricarbonyl.* A mixture of 3·4 g (6·7 mmole) of triiron dodecacarbonyl, and 5 ml (~41 mmole) of 1,5-cyclo-octadiene dissolved in 40 ml of benzene was refluxed for 12 hr under nitrogen. After cooling the mixture to room temperature, filtration under nitrogen, and removal of benzene at 20 mm a brown oil remained. This oil was placed in a sublimation apparatus and maintained at 25°/0·1 mm for 4 hr. Sublimation (35–60°/0·1 mm) was then carried out, with the probe of the sublimer cooled to −78°. The sublimate, 500 mg (10 per cent yield) of 1,5-cyclo-octadiene–iron tricarbonyl, was stored under nitrogen at −78°. Found: C, 54·2; H, 5·1. Calc. for $C_{11}H_{12}O_3Fe$: C, 53·0; H, 4·8%). 1,5-Cyclo-octadiene–iron tricarbonyl is an orange liquid which forms a yellow solid just below ambient temperature. Even under nitrogen it quickly decomposes making microanalysis very difficult. The infra-red spectrum taken in carbon disulphide shows carbonyl bands at 2080, 2010 and 1977 cm^{-1}.

3. *Reaction between triiron dodecacarbonyl and 1,4-pentadiene.* A mixture of triiron dodecacarbonyl (5·4 g, 11 mmole), and 1,4-pentadiene (5·2 ml, 50 mmole) dissolved in 150 ml of 2,2,4-trimethylpentane (b.p. 99°) was refluxed under nitrogen for 10 hr. The mixture was cooled to room temperature, filtered under nitrogen, and evaporated at 15 mm to give a yellow-brown oil. The latter was sublimed (60–70°/0·3 mm) with the probe of the sublimation apparatus at −78°. Since the product did not solidify at −78°, it was necessary to remove product from the probe frequently. Resublimation (25°/0·3 mm) yielded 1·0 g (15 per cent yield) of yellow liquid $C_5H_8{\cdot}Fe(CO)_3$ (Found: C, 46·1; H, 3·8. Calcd. for $C_8H_8O_3Fe$: C, 46·2; H, 3·8%). The analytical sample was held at 25°/0·3 mm for 10 min. The compound is so volatile that if held at such a reduced pressure for a

* Since the work described in this paper was completed, the reaction between thiophene and iron carbonyls has been reinvestigated and shown[11] to give a product containing no sulphur but having the same melting point as that reported[4] for thiophene-iron dicarbonyl.

[11] H. KAESZ, R. B. KING, T. A. MANUEL, L. D. NICHOLS and F. G. A. STONE, *J. Amer. Chem. Soc.* **82**, 4749 (1960).
[12] W. HIEBER, *Z. Anorg. Chem.* **204**, 165 (1932); W. HIEBER and G. BRENDEL, *Ibid.* **289**, 324 (1957).
[13] M. W. RIGG and R. ROSENTHAL, *J. Amer. Chem. Soc.* **71**, 2865 (1949).
[14] G. I. KUZNETSOVA, *Uchenye Zapiski Saratov. Gosudarst. Univ. N. G. Chernyshevskogo, Sbornik. Nauch. Trudov. Studentov* 80 (1939). *Chem. Abstr.* **35**, 6236 (1941).
[15] A. BRUYLANTS and J. ROWIES, *Bull. Soc. Chim. Belg.* **59**, 244 (1950).
[16] A. P. KRAPCHO, Thesis, Harvard University (1957).

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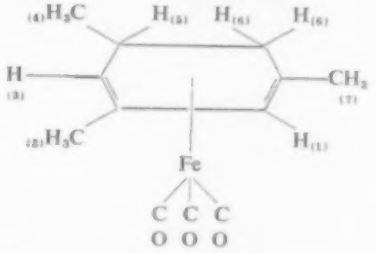
longer time considerable loss of sample will occur. The infra-red spectrum taken in carbon disulphide solution shows C—O bands at 2052 and 1980 cm^{-1}. An infra-red spectrum of a liquid film (0·015 mm) of the complex $C_5H_8{\cdot}Fe(CO)_3$ showed, in addition to very strong carbonyl absorptions, strong bands at 2967, 1451, 1381, 1030 and 667 cm^{-1}.

A 300 mg (1·44 mmole) sample of $C_5H_8{\cdot}Fe(CO)_3$ was heated with excess of triphenylphosphine in an evacuated Pyrex bulb for 15 hr at 150°. On opening the bulb to the vacuum line fractionation afforded 0·933 mmole (65 per cent of theory) of gas, the infra-red spectrum of which was identical with the published[17] spectrum of *trans*-1,3-pentadiene. In a series of independent experiments, 1,4-pentadiene itself was heated at 160° with triphenylphosphine and with bis-(triphenylphosphine) iron tricarbonyl (product of the reaction between $C_5H_8{\cdot}Fe(CO)_3$ and triphenylphosphine). No rearrangement of 1,4-pentadiene to 1,3-pentadiene took place under these conditions.

4. *Reaction between triiron dodecacarbonyl and 1,4-dihydromesitylene.* Triiron dodecacarbonyl (3·4 g, 6·8 mmole), and 4·2 g of a mixture[16] containing mesitylene, tetrahydromesitylene, and 32% 1,4-dihydromesitylene (1·3 g, 10·1 mmoles) dissolved in 40 ml benzene was refluxed under nitrogen for 19 hr. Filtration and evaporation of the filtrate, followed by chromatography with pentane, gave a yellow oil, which was further purified by sublimation (35°/0·1 mm), yielded 310 mg (12 per cent yield) of complex (Found: C, 55·2; H, 5·4. Calc. for $C_{12}H_{14}O_3Fe$: C, 55·0; H, 5·4%). The compound possesses carbonyl stretching frequencies at 2037 cm^{-1} and 1969 cm^{-1} in carbon disulphide solution. The nuclear magnetic resonance spectrum indicates that the iron tricarbonyl complex lacks the two-fold symmetry expected of a 1,4-hexadiene derivative. The spectrum finds a reasonable



VI

explanation in terms of structure (VI). Relative to the low-field side of tetramethylsilane, proton resonances occur at 5·17 p.p.m. (assigned to $H_{(1)}$, analogous to the positions of similar protons in isoprene– and butadiene–iron tricarbonyl), 2·92 p.p.m. (assigned to $H_{(5)}$), 2·15 p.p.m. and shoulder on peak at 2·07 p.p.m. (assigned to $=CH_{2(6)}$), 2·07 p.p.m. (assigned to protons $H_{(2)}$, analogous to position of CH_3 proton resonance in isoprene–iron tricarbonyl), 1·55 p.p.m. (assigned to protons $H_{(7)}$), 0.93 p.p.m. (doublet, protons $H_{(4)}$ split by $H_{(5)}$). The peak due to $H_{(3)}$ must lie either under the standard peak or that at 1·55 p.p.m. if its chemical shift is analogous to that of similar protons in isoprene– or butadiene–iron tricarbonyl.

5. *Isoprene–iron tricarbonyl.* A mixture of isoprene (60 ml, 600 mmole) and iron pentacarbonyl (60 ml, 447 mmole) was irradiated with a sun lamp for 44 hr. The resulting orange solution was concentrated and chromatographed on alumina. Elution with isohexane gave an orange eluate. The eluate was evaporated, but the infra-red spectrum of the remaining oil showed a band at 1640 cm^{-1} characteristic of an unsaturated impurity. The oil was, therefore, re-chromatographed four additional times. Evaporation of the final eluate yielded 1·0 g of a yellow liquid, having no band in its infra-red spectrum at 1640 cm^{-1}. The yield of pure isoprene–iron tricarbonyl was only 1 per cent, but the long purification procedure introduced considerable losses. Isoprene–iron tricarbonyl (Found: C, 46·3; H, 3·8. Calc. for $C_8H_8O_3Fe$: C, 46·2; H, 3·8%) has carbonyl bands in its infra-red spectrum (carbon disulphide solution) at 2049 and 1980 cm^{-1}. The infra-red spectrum taken as a liquid film (0·015 mm) has, besides the carbonyl absorptions, principal bands at 3003 (*m*), 2941 (*m*), 1481 (*s*), 1443 (*m*, *sh*), 1429 (*s*), 1379 (*s*), 1170 (*m*), 1060 (*w*), 1033 (*s*), 990 (*w*), 972 (*w*), 939 (*w*), 922 (*w*), 819 (*m*), 797 (*w*), 771 (*w*) cm^{-1}.

The nuclear magnetic resonance spectrum of isoprene–iron tricarbonyl is quite analogous to that reported[18] for butadiene–iron tricarbonyl, indicating the similarity of the bonding in the two

[17] *Catalog of Infra-red Spectral Data.* American Petroleum Institute Research Project 44.
[18] M. L. H. GREEN, L. PRATT and G. WILKINSON, *J. Chem. Soc.* 3753 (1959).

complexes. Relative to low-field side of tetramethylsilane, resonances occur at 4·98 p.p.m. (relative intensity 1, ascribed to $H_{(3)}$) and 2·15 p.p.m. (relative intensity 3, ascribed to methyl group protons), as well as groups of peaks (relative intensity 2 for each group) at 1·7, 1·5 p.p.m. and 0·42, 0·28, 0·05 p.p.m. (ascribed to the $=CH_2$ protons). Butadiene–iron tricarbonyl displays peaks at 5·28 p.p.m., 1·68 p.p.m. and 0·22 p.p.m.[10]

6. *Reaction between α-terpinene and triiron dodecacarbonyl.** A mixture of α-terpinene (1·1 g, 8·1 mmole), and triiron dodecacarbonyl (4·0 g, 8 mmole) dissolved in 40 ml benzene was refluxed under nitrogen for 15 hr. Filtration followed by evaporation of solvent gave a yellow oil which was chromatographed on alumina with pentane. Evaporation of the eluate gave a yellow-orange oil which was purified by sublimation (50°/0·1 mm). In this manner 450 mg (20 per cent yield) of α-terpinene–iron tricarbonyl was obtained. (Found: C, 56·5; H, 5·8. Calc. for $C_{13}H_{16}O_3Fe$: C, 56·5; H, 5·8%).

The infra-red spectrum of α-terpinene–iron tricarbonyl (carbon disulphide solution) exhibits carbonyl absorptions at 2037 and 1965 cm^{-1}. In addition the spectrum of a liquid film of the complex had principal bands at 2950 (*s*), 2882 (*s*), 1464 (*s*), 1445 (*s*), 1377 (*s*), 1362 (*m*), 1335 (*m*), 1300 (*w*), 1232 (*w*), 1195 (*s*), 1182 (*w, sh*), 1160 (*vw*), 1082 (*m*), 1062 (*w*), 1036 (*s*), 1014 (*w*), 986 (*m*), 927 (*vw*), 890 (*w*), 872 (*m*), 824 (*m*), 749 (*m*), 658 (*s*) cm^{-1}.

7. *Reaction between iron pentacarbonyl and isoprene at high temperature.*[11] A stainless-steel bomb, 150 ml capacity, was loaded with isoprene (20 ml., 0·2 mole) and iron pentacarbonyl (25 ml, 0·18 mole), and heated at 155° for 16 hr. After cooling the bomb to room temperature carbon monoxide pressure was released, the mixture filtered, and excess of reactants removed at 3 mm through a 40 cm Vigreaux column. The remaining liquid was chromatographed on alumina, a yellowish band eluted with isohexane, and the resulting golden-yellow solution concentrated to 6·4 g of an orange liquid. Analysis of this liquid (Found: C, 58·4; H, 5·8%), as well as its infra-red spectrum (in carbon disulphide solution carbonyl bands at 2049, 2037 and 1972 cm^{-1} were observed), showed that it was a mixture of isoprene–iron tricarbonyl, α-terpinene–iron tricarbonyl and hydrocarbon impurity.

In similar reactions to that described here it was possible to isolate isoprene–iron tricarbonyl by repeated chromatography. However, α-terpinene–iron tricarbonyl could not be completely separated from hydrocarbon impurities in these cases.

8. *Alloöcimene–iron tricarbonyl.* A mixture of alloöcimene (2·4 g, 18 mmole) and triiron dodecacarbonyl (5·0 g, 10 mmole) dissolved in 40 ml benzene was refluxed under nitrogen for 22 hr. Filtration and evaporation of the filtrate left an orange oil, which was chromatographed on alumina. Evaporation of the yellow eluate left an orange oil, which was sublimed at 60°/0·2 mm. The oily sublimate was dissolved in pentane and cooled to −78°. Filtration gave 320 mg (6·4 per cent yield) of alloöcimene–iron tricarbonyl, golden crystals of m.p. 47–48°. (Found: C, 56·2: H, 5·9; Fe, 19·3 Calc. for $C_{13}H_{16}O_3Fe$: C, 56·5; H, 5·8; Fe, 20·2%).

A 64·2 mg (0·23 mmole) sample of alloöcimene–iron tricarbonyl dissolved in 6 ml toluene and treated with 400 mg iodine, dissolved in 6 ml water containing potassium iodide, afforded 13·7 cm^3 (S.T.P.) of carbon monoxide (88 per cent of 3 mole of carbon monoxide per mole of complex).

Degradation of a 400 mg sample of alloöcimene–iron tricarbonyl with triphenylphosphine in a bulb at 150° for 50 hr afforded a liquid, the infra-red and ultra-violet spectra of which corresponded to those of alloöcimene. Solid remaining in the bulb consisted of excess triphenylphosphine and *trans*-bis(triphenylphosphine)iron tricarbonyl, identified by its infra-red spectrum.[7]

The infra-red spectrum of alloöcimene–iron tricarbonyl in carbon disulphide solution showed carbonyl absorptions at 2028 and 1963 cm^{-1}, and a band in the carbon–carbon double bond region at 1653 cm^{-1}.

9. *Preparation of the compounds* $(CH_3CH{:}CHCH{:}CHR)Fe(CO)_3$. A mixture of 1·8 g (3·6 mmole) of triiron dodecacarbonyl, 5 mmole of the substituted 1,3-pentadiene and 40 ml of thiophene-free benzene was refluxed under nitrogen for about 10 hr or until the green colour of the iron carbonyl was discharged. After cooling to room temperature filtration usually afforded a yellow solution. Solvent was removed *in vacuo* and the yellow liquid dissolved in isohexane, filtered, and the filtrate cooled to −78°. Yellow crystals of the product separated which in the case of $(CH_3CH{:}CHCH{:}CHCN)Fe(CO)_3$ and $(CH_3CH{:}CHCH{:}CHCHO)Fe(CO)_3$ melted before reaching room temperature. The product was held briefly at 25°/0·1 mm before being submitted for analysis.

* We are indebted to Drs. L. A. GOLDBLATT, R. V. LAWRENCE and N. T. MIROV of the U.S. Department of Agriculture for supplying us with pure samples of the terpenes used in our work.

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For the preparation of $(CH_3CH{:}CHCH{:}CHCONH_2)Fe(CO)_3$ the procedure was somewhat different. The yellow benzene solution obtained from the reaction was treated with excess of isohexane and the yellow solid produced filtered. This solid was sublimed (100°/0·1 mm) to give sorbamide–iron tricarbonyl.

Analytical and other data for these new compounds are as tabulated.

Compound[a]	m.p. and colour (°C)	Carbon (%)		Hydrogen (%)		Metal carbonyl bands (cm^{-1}) in infra-red spectra, CS_2 solution
		Calc.	Found	Calc.	Found	
$(C_5H_7CO_2C_2H_5)Fe(CO)_3$	49–51 yellow	47·1	46·9	4·3	4·3	2065, 1995[b]
$(C_5H_7CONH_2)Fe(CO)_3$	132–134 yellow	43·0	43·0	3·6	3·6[c]	2065, 1995[d]
$(C_5H_7COCH_3)Fe(CO)_3$	31–33 yellow	48·0	47·5	4·3	4·2	2065, 2000[e]
$(C_5H_7CN)Fe(CO)_3$	yellow liquid	46·3	46·5	3·0	3·1[f]	2070, 2000[g]
$(C_5H_7CHO)Fe(CO)_3$	orange liquid	45·8	46·5	3·4	3·5	2070, 2000[h]

[a]C_5H_7 represents the $CH_3CH{:}CHCH{:}CH$- group. [b]Ester carbonyl band, 1717 cm^{-1}. [c]% N, calc., 5·6; found, 5·7. [d]Amide carbonyl band, 1686 cm^{-1}. [e]Ketonic carbonyl band, 1686 cm^{-1}. [f]% N, calc., 6·0 found, 6·1. [g]Cyanide band at 2235 cm^{-1}. [h]Aldehyde carbonyl band, 1690 cm^{-1}.

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RHENIUM CO-ORDINATION COMPOUNDS—I

HALOGENOTRIPHENYLPHOSPHINERHENIUM AND HALOGENO-TRIPHENYLPHOSPHINECARBONYLRHENIUM COMPOUNDS*

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Abstract—Using $HReO_4$ and PR_3 in ethyl alcohol, as starting material, with hydrohalic acids, we obtained directly the Re(III) compound $Re(PR_3)_2Cl_3$, with hydrochloric acid; with hydrobromic and hydroiodic acids the Re(II) compounds $Re(PR_3)_2Br_2$, $Re(PR_3)_2I_2$.

The compound $Re(PR_3)_2Cl_2$ can only be obtained using a reducing reagent such as hydrazine hydrochloride, while $Re(PR_3)_2Br_2$ and $Re(PR_3)_2I_2$ can be prepared from the corresponding compounds of Re(II) by oxidation with bromine and iodine. Likewise $Re(PR_3)_2Cl_3$ can be obtained from $Re(PR_3)_2Cl_2$ with chlorine, while by reaction between $ReCl_3$ and PR_3 the compound $Re(PR_3)Cl_3$ is formed.

By the reaction of carbon monoxide at high pressure with these compounds, Re(I) carbonyl derivatives have been isolated: the above mentioned chloro compounds gave $Re(PR_3)_2(CO)_2Cl$, $Re(PR_3)_2(CO)_2Cl$.

$Re(PR_3)_2Br_2$ gave $Re(PR_3)_2(CO)_2Br$, and $Re(PR_3)_2(CO)_2Br$, under the same conditions, while to date, we have obtained only the Re(I) monocarbonyl iodide derivative, $Re(PR_3)_2(CO)I$.

All these compounds are diamagnetic in the solid state; but the derivatives of Re(II) have the paramagnetism corresponding to one electron spin in chloroform solution.

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ONLY a small number of rhenium co-ordination compounds with ligands able to give bonds with some π-character have been reported so far, i.e. the ditertiary arsine compounds described by NYHOLM[1], some carbonyl derivatives reported by HIEBER[2], and WILKINSON[3], and the bipirydyl compound of JEZOWSKA[4].

As it was likely that rhenium would form low-valent complexes with ligands of π-type, we studied the addition compounds of rhenium halides with triphenylphosphine and their carbonyl-derivatives.

EXPERIMENTAL SECTION

Dichlorobis(triphenylphosphine)rhenium(II). One gramme perrhenic acid, 1 g hydrazinium chloride and 5 g triphenylphosphine (30 ml) are refluxed in ethanol for a few minutes. The compound which precipitates is dissolved in hot benzene and recrystallized by addition of ethanol: m.p. (dec.) 166°C. (Found: Re, 23; Cl, 9·0; P, 7·6; mol. wt. 760. Calc. for $C_{36}H_{30}Cl_2P_2Re$: 23·8; Cl, 9·1; P, 7·9%; mol. wt. 782—mol. wt. by cryoscopy in $1·4 \times 10^{-2}$ M bromoform solution).

Dibromobis(triphenylphosphine)rhenium(II). One gramme perrhenic acid in ethanol (5 ml) and 2 ml hydrobromic acid are boiled for about 5 min and a hot saturated ethanolic solution of 5 g triphenylphosphine is added. On cooling, violet crystals precipitate which are recrystallized from

* This research has been reported at the IUPAC Congress in Munich 1959.[5]

[1] N. F. CURTIS, J. E. FERGUSSON and R. S. NYHOLM, *Chem. & Ind.* 625 (1958); S. E. FERGUSSON and R. S. NYHOLM, *Chem. & Ind.* 1555 (1958).
[2] W. HIEBER and L. SCHUSTER, *Z. Anorg. Chem.* **287**, 214 (1956).
[3] E. W. ABEL and G. WILKINSON, *J. Chem. Soc.* 1501 (1959).
[4] B. JEZOWSKA, Traebiatowska, IUPAC Congress Abstr. 77. London (1959).
[5] M. FRENI and V. VALENTI, IUPAC Congress Abstr. A1057. Munich (1959).

benzene plus ethanol: m.p. (dec.) 144°C. (Found: Re, 20·1; Br, 18·1; P, 6·9; mol. wt. 830. Calc. for $C_{36}H_{30}Br_2P_2Re$: Re, 21·4; Br, 18·4; P, 7·1%; mol. wt. 870—mol. wt. by cryoscopy in 10^{-3} M bromoform solution).

Diiodobis(triphenylphosphine)rhenium(II). Prepared as above from perrhenic acid, hydroiodic acid and phosphine in ethanol. The greenish needle-like crystals are recrystallized from benzene plus ethanol: m.p. (dec.) 162°C. (Found: Re, 19·1; I, 26·8; P, 6·5; mol. wt. 920. Calc. for $C_{36}H_{30}I_2P_2Re$: Re, 19·3; I, 26·3; P, 6·4%: mol. wt. 965—mol. wt. in 10^{-3} M bromoform solution). The same compound is obtained when a saturated solution of K_2ReI_6 (2 g) in acetone is allowed to react with a saturated solution of triphenylphosphine in acetone (3 g). A red needle-like crystalline compound is first obtained, which rapidly discolours even in an inert atmosphere. By recrystallization the previously described compound is obtained: m.p. (dec.) 162°C. (Found: Re, 19·5; I, 26·1; P, 6·2%).

Trichlorotriphenylphosphinerhenium(III). A saturated solution of $ReCl_3$ (2 g) in ethanol is allowed to react with a cold saturated solution of triphenylphosphine (4 g) in ethanol. A dark red precipitate is formed, which is recrystallized from methylene chloride plus hexane: m.p. (dec.) 230°C. (Found: Re, 34·0; Cl, 19·3; P, 5·5. Calc. for $C_{18}H_{15}Cl_3PRe$: Re, 33·6; Cl, 19·2; P, 5·6%).

Trichlorobis(triphenylphosphine)rhenium(III). One gramme perrhenic acid 2 ml hydrochloric acid and a hot saturated ethanol solution of 5 g triphenylphosphine are refluxed for about 5 min. The yellow crystalline precipitate is dissolved in benzene and precipitated by hexane: m.p. (dec.) 220°C. (Found: Re, 23·2; Cl, 12·8; P, 7·4. Calc. for $C_{36}H_{30}Cl_3P_2Re$: Re, 22·8; Cl, 13·0; P, 7·6%). The same compound is obtained from a solution of 0·8 g $ReCl_2(PR_3)_2$ in methylene chloride by addition of 10 ml M/10 chlorine solution in the same solvent. Recrystallized from benzene: m.p. (dec.) 220°C. (Found: Re, 22·8; Cl, 13·1; P, 7·2%).

Tribromobis(triphenylphosphine)rhenium(III). A benzene solution of 0·9 g $ReBr_2(PR_3)_2$ (mmole) is reacted with 20 ml 0·05 M bromine in benzene. The yellow crystalline product which separates at once is dissolved in chloroform and precipitated with hexane: m.p. (dec.) 193°C. (Found: Re, 20·0; Br, 25·6; P, 6·4; Calc. for $C_{36}H_{30}Br_3P_2Re$: Re, 19·6; Br, 25·3; P, 6·5%).

Triiodobis(triphenylphosphine)rhenium(III). Prepared as the previous compound from $ReI_2(PR_3)_2$ and iodine: m.p. (dec.) 174°C. (Found: Re, 17·4; I, 35·3; P, 5·6. Calc. for $C_{36}H_{30}I_3P_2Re$: R, 17·0; I, 34·8; P, 5·7%).

Chlorodicarbonylbis(triphenylphosphine)rhenium(I). (a) A mixture of 0·56 g $ReCl_3(PR_3)$ (1 mmole) and 0·8 g PR_3 (3 mmole) is kept in a pressure vessel under 200 atm of CO (initial pressure) at 120°C for 12 hr in the presence of metallic copper. On extracting the reacted mass with methylene dichloride and precipitating with ethanol, pink hexagonal plates (0·50 g = 62 per cent yields) are obtained which are recrystallized from hot benzene: m.p. (dec.) 202°C. (Found: Re, 24·0; Cl, 4·6; P, 7·7; CO, 6·9; mol. wt. 850·0. Calc. for $C_{38}H_{30}P_2(CO)_2ClRe$: Re, 23·2; Cl, 4·4; P, 7·7; CO, 7·0; mol. wt. 802·5).

(b) The same product is obtained in much lower yields both from $ReCl_2(PR)_2$ and $ReCl_3(PR_3)_2$, at 120°C and 200 atm CO (initial pressure), in presence of metallic copper. When the reacted mass is extracted with benzene and the solution precipitated with ethanol the pink $ReCl(CO)_2(PR_3)_2$ separates. m.p. 202°C. When these pink crystals are boiled for about 10 min with a 10 per cent solution of *p*-toluidine in benzene, they yield an ivory white crystalline compound, all physical and chemical features of which are identical with those of the original pink compound. The Debye patterns of the two compounds are also identical. The ivory white compound is also obtained on crystallizing the pink compound from benzene in the presence of a small amount of potassium hydroxide.

Chlorotricarbonylbis(triphenylphosphine)rhenium(I). From $ReCl(CO)_2(PR_3)_2$ with CO at 200 atm and 200°C for 24 hr. The mass is extracted with benzene and reprecipitated with ethanol. The ivory yellow needle-like crystals are purified by recrystallization from the same solvents: m.p. (dec.) 183°C. (Found: Re, 22·0; Cl, 4·4; P, 7·6; CO, 10·0. Calc. for $C_{38}H_{30}P_2(CO)_3ClRe$: Re, 22·4; Cl, 4·3; P, 7·5; CO, 10·0%).

Bromodicarbonylbis(triphenylphosphine)rhenium(I). (a) One gramme $ReBr_3(PR_3)_2$ and 0·5 g PR_3 are treated under a pressure of 200 atm of CO for 12 hr in the presence of metallic copper. The orange mass is extracted with hot benzene and then precipitated with ethanol. Orange crystals are obtained (0·80 g = 82 per cent yields). This compound, like the corresponding chloride, becomes yellow when recrystallized from an alkaline solution. It is stable to air indefinitely: m.p. (dec.)

193°C. (Found: Re, 21·2; Br, 9·8; P, 7·8; CO, 6·6; mol. wt. 820. Calc. for $C_{36}H_{30}P_2(CO)_2BrRe$: Re, 22·0; Br, 9·5; P, 7·3; CO, 6·6%; mol. wt. 846—mol. wt. by cryoscopy in 10^{-2} M bromoform solution).

(b) The same $ReBr(CO)_2(PR_3)_2$ is obtained in much lower yields from $ReBr_3(PR_3)_2$ at 120°C and 200 atm CO. The yellow pasty mass extracted with hot benzene is precipitated by ethanol, Orange crystals: m.p. (dec.) 193°C. (Found: Re, 21·85; Br, 9·4; P, 7·0; CO, 6·7%).

Bromotricarbonylbis(triphenylphosphine)rhenium(I). Obtained from $ReBr(CO)_2(PR_3)_2$ with CO at 200 atm and 200°C for 30 hrs, the mass is extracted with benzene, and the solvent evaporated to dryness. On addition of ethanol, white needle-like crystals are obtained which are recrystallized from the same solvent: m.p. (dec.) 142°C. Found: Re, 21·9; Br, 9·7; P, 7·00; CO, 9·7; Calc. for $C_{36}H_{30}P_2(CO)_3BrRe$: Re, 21·3; Br, 9·2; P, 7·1; CO, 9·6%)

Iodomonocarbonylbis(triphenylphosphine)rhenium(I). One gramme $ReI_2(PR_3)_2$ and 0·5 g PR_3 are treated with CO at 200 atm and 80°C for 12 hr in the presence of metallic copper. The blue mass is extracted with benzene and then precipitated with ethanol. Blue crystals (0·3 g): m.p. (dec.) 198°C. (Found: Re, 21·0; I, 14·7; P, 7·0; CO, 3·2; mol. wt. 900. Calc. for $C_{36}H_{30}P_2COIRe$: Re, 21·5; I, 14·7; P, 7·2; CO, 3·2% mol. wt. 866—mol. wt. by cryoscopy in 10^{-2} M bromoform solution).

Analysis. Rhenium was determined as tetraphenyl arsonium perrhenate after alkaline oxidation of the complexes by the Parr method. The results obtained (±6 per cent) in this way were far from satisfactory. Later more satisfactory analyses were conducted by oxidizing the complexes with fuming nitric acid by the Carius method.

Physical determinations

The *magnetic susceptibilities* were measured with a semimicrobalance using the Gouy method.[6] Measurements on solid compounds were corrected for their diamagnetic susceptibility using correction constants from SELWOOD[7]

The *electric moments* were calculated with the approximate formula of COHEN and HENRIQUEZ[8] from the dielectric constants of the dilute benzene solutions, measured with the Dipolmeter DM 01 and the cell DFL 2 of the firm Wissenschaftlich Technische Werkstätten of Weilheim/Oberbayern.

The *molecular weights* were determined by cryoscopy in nitrobenzene or bromoform.

The *conductivities* were determined on the 2×10^{-2} M nitrobenzene solutions with Kohlrausch method, using a cell with large palladium electrodes to increase the sensitivity.

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DISCUSSION

It appears that two stable addition compounds of rhenium halides with triphenylphosphine (PR_3) may be obtained, of the type $ReX_2(PR_3)_2$ and $ReX_3(PR_3)_2$. Using as starting material the high-valent rhenium compounds, in the presence of an excess of phosphine and of the corresponding halogen acids, the divalent compounds are obtained when X is Br or I, and with Cl the trivalent one is formed. As triphenylphosphine, which is always present in excess in these preparations, is a reducing agent stronger than hydroiodic and hydrobromic acids, it must be admitted that $ReI_3(PR_3)_2$ and $ReBr_3(PR_3)_2$ are more easily reduced than $ReCl_3(PR_3)_2$.

$ReCl_2(PR_3)_2$ is only obtained in the presence of hydrazinium chloride while the bromo and iodo derivatives of trivalent rhenium can be prepared with the calculated amounts of halogens on the divalent compounds. The compounds $ReX_2(PR_3)_2$, though coordinatively unsaturated do not tend to coordinate any more phosphine molecules.

The lack of conductivity is consistent with their formulation. They probably have a square planar structure with a *cis* configuration as indicated by their dipole moment.

The magnetic moment in solution is very near to the value for one unpaired electron as expected for divalent rhenium (d^5).

[6] A. WEISSBERGER, *Physical Methods of Organic Chemistry* Vol. 2 p. 1221. Interscience, New York (1946).
[7] P. S. ELWOOD, *Magnetochemistry* p. 78. Interscience, New York (1956).
[8] P. C. HENRIQUEZ, *Physica* **1**, 41 (1934).

The diamagnetic behaviour in the solid may be attributed to a direct interaction between the metal atoms or to a Re^{I}–Re^{III} mesomerism reached through halogen bridges.

The Re^{III} compounds $ReX_3(PR_3)_2$ are also non-electrolytes their very poor solubility can be taken as an indication that they are dimeric and, if so, they are octahedral and coordinatively saturated. They are not affected by halogens, which shows that in

Compound*	Colour	χ_M at 22°C of the solid (cm^3/mole)	Solubility‡	Molecular conductivity in nitrobenzene 2×10^{-3} M ($ohm^{-1}cm^2$)
$Re(PR_3)_2(CO)_2Cl$	ivory	-235×10^{-6}	*v.s.* chloroform, methylene chloride *sl.* benzene, nitrobenzene *i.* alcohol, ether, acetone	<0·1
$Re(PR_3)_2(CO)_3Cl$	ivory yellow	-230×10^{-6}		<0·1
$Re(PR_3)_2(CO)_2Br$	orange yellow	-240×10^{-6}		<0·1
$Re(PR_3)_2(CO)_3Br$		-250×10^{-6}	*v.s.* chloroform, methylene chloride, benzene, nitrobenzene *i.* other solvents	<0·1
$Re(PR_3)_2COI$	blue	-270×10^{-6}		<0·05

* PR_3 = triphenylphosphine
† on the compound in chloroform solution
‡ *v. s.* = very soluble; *s.* = soluble; *sl.* = slightly soluble; *i* = insoluble
** The first value is obtained on the compound immediately after its preparation; the second value is obtained after some time

this case the oxidation state 3+ of rhenium is remarkably stable. They are diamagnetic as expected for low spin Re^{III} compounds. No satisfactory explanation for the paramagnetism of the labile form of $ReCl_3(PR_3)$, which has been checked in all the preparations of this compound has been suggested.

The action of CO on these compounds gives in all cases the Re^{I} derivatives, containing two molecules of phosphine and from one to three molecules of CO. The reaction takes place at about 100°C, that is at a temperature much lower than necessary to introduce CO in other rhenium derivatives. The compounds of the type $ReX(CO)_3(PR_3)_2$ had been obtained independently by HIEBER[2] and WILKINSON[3], from $ReX(CO)_5$ and the phosphine at 120°C.

The fact that the same compounds are obtained from opposite directions shows that they represent the most stable substitution products of the phosphine on the rhenium carbonyl halides.

The stabilization of the monovalent state of rhenium is achieved through the bonding of at least two molecules of CO in the chloride and the bromide and of only one CO in the iodide.

This seems to indicate that the stabilization of Re^{I} is obtained most easily for the iodocompound, while in the case of the halocarbonyliridiates(I)[9] the iodocompound is the most readly oxidized. These d^6 compounds are diamagnetic; the hexaco-ordinated $ReX(CO)_3(PR_3)_2$ are probably octahedral; the pentacoordinated $ReX(CO)_2(PR_3)_2$ can be square pyramids (d^2sp^2) or trigonal bipyramids (dsp^3), while the tetra-coordinated $ReICO(PR_3)_2$ should be planar. The latter compound is a typical example of the

[9] M. ANGOLETTO, *Gazz. Chim. Ital.* **90**, In press (1960).

Compound*	Colour	X_M at 22°C of the the solid (cm^3/mole)	X_M at 22°C of the chlorof. solution (cm^3/mole)	Effective magnetic moment in solution	Electric moment	Solubility‡	Molecular conductivity in nitrobenzene 2×10^{-3} M (ohm^{-1} cm^2)
$Re\ Cl_2(PR_3)_2$	violet prisms	-260×10^{-6}	1210×10^{-6}	1·7 B.M.†	3·3 D	*v.s.* chloroform, benzene	<0·10
$Re\ Br_2(PR_3)_2$	violet prisms	-220×10^{-6}	1200×10^{-6}	1·7 B.M.†	3·3 D	*sl.* dioxane	<0·10
$Re\ I_2(PR_3)_2$	greenish needles	-200×10^{-6}	1190×10^{-6}	1·7 B.M.†	3·3 D	*i.* alcohol, ether, acetone	<0·05
$Re\ Cl_3(PR_3)$	dark-red needles	800×10^{-6}** -120×10^{-6}**		1·6 B.M.		*sl.* chloroform, methylene chloride, benzene, nitrobenzene *i.* other solvents	<0·10
$Re\ Cl_3(PR_3)_2$	yellow-	-250×10^{-6}					<0·10
$Re\ Br_3(PR_3)_2$	yellow	-265×10^{-6}					<0·10
$Re\ I_2(PR_3)_2$	brick-red	-280×10^{-6}					<0·05

* PR_3 = triphenylphosphine
† on the compound in chloroform solution
‡ *v.s.* = very soluble; *s.* = soluble; *sl.* = slightly soluble; *i.* = insoluble
** The first value is obtained on the compound immediately after its preparation; the second value is obtained after some time.

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stability that can be reached by heavy transition metals in a co-ordinatively unsaturated state. It was not obtained by WILKINSON[3] by displacing carbon monoxide with phosphine in the iodopentacarbonylrhenium(I). He prepared instead $ReI(CO)_3(PR_3)_2$.

On the other hand we could not prepare the iododerivative with more than one CO molecule, because at higher temperatures only $ReI(CO)_5$ is formed. That would prove that the phosphine is more firmly bound to the chloro- and bromo- than to the iododerivative.

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PREPARATION, PHYSICAL PROPERTIES AND INFRA-RED STUDIES OF SEVERAL ALKYL AND ARYL PHOSPHORIC ACIDS*†

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(*Received* 21 *April* 1960)

Abstract—Several alkyl and aryl phosphoric acids of the type $(GO)_2PO(OH)$‡ have been prepared. The physical properties of these compounds, including cryoscopic molecular weights and infra-red spectra are presented. The cryoscopic and infra-red data indicate the existence of strong intermolecular hydrogen bonding in these compounds, and it is postulated that such strong hydrogen bonding is typical of this class of acids. Attempts are made to analyse the infra-red spectra of the aryl phosphoric acids in terms of vibrations involving the phosphorus atom and those involving the benzene ring.

A NUMBER of organophosphoric acids of the type $(GO)_2PO(OH)$ have been prepared in our laboratories. Several of these were shown to be dimeric in benzene and to display strong intermolecular hydrogen bonding.[1] This paper describes the preparation, physical properties and infrared spectra of several additional acids of this class, some of which are presumed to be new.

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EXPERIMENTAL

Preparation

The neutral phosphates $(GO)_3PO$, where G is β-naphthyl, β-phenylethyl, γ-phenylpropyl, *p*-phenylphenyl, *p*-isopropylphenyl or cyclohexyl were prepared from $POCl_3$ and the respective alcohol. The neutral phosphates, where G is *p*-tolyl and *o*-tolyl, were obtained from Eastman Kodak Company. Tri(n-butoxyethyl)-phosphate was obtained from Ohio Apex Co. The neutral phosphates were hydrolyzed by refluxing with aqueous 10% NaOH (50 per cent excess) for periods up to 8 hr. The sodium salts of the monobasic acids, obtained on hydrolysis, were separated from the neutral phosphates by the procedure described in a previous publication.[1] The separation from GOH was also accomplished by this previously described procedure, except for the β-naphthyl and *p*-tolyl compounds and for the *o*-tolyl compound, in which cases separation of the GOH was achieved by fractional recrystallization and by vacuum distillation, respectively.

The elemental analyses for carbon and hydrogen are listed in Table 1.

Physical properties

The equivalent weights of the compounds discussed in this paper were obtained by standard alkali titration. Viscosity measurements were made at a constant temperature, controlled at $20° \pm 0{\cdot}025°C$. Water contents were determined by standard Karl Fischer titration. Table 2 lists the physical properties of these solvents.

Cryoscopic measurements were conducted in a Beckman type freezing-point apparatus using a Beckman differential thermometer. The benzene (Spectral Grade), α-camphor and the naphthalene

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.
† Paper presented at the 11th Annual Society of Spectroscopy Symposium in Chicago, June, 1960.
‡ G may be aryl, alkyl or mixed alkyl-aryl or a substituted variant of one of these.

[1] D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg Nucl. Chem.* **7**, 231 (1958); **4**, 371 (1957); **10**, 275 (1959).

were obtained from Eastman Kodak Co. The acetic acid (Analytical Reagent) was obtained from Mallinckrodt Chemical Works. The method of determination of the freezing-point constants has been discussed previously.[1] The results of the molecular weight determinations are shown in Table 3.

The absorption measurements were obtained by means of a Beckman IR-4 spectrophotometer using a sodium chloride prism. Spectra were obtained on liquid film and KBr disks. The KBr disk spectra were always checked by Nujol mull spectra.

TABLE 1.—C AND H ELEMENTAL ANALYSES OF $(GO)_2PO(OH)$

G	C		H*	
	Theory	Found	Theory	Found
β-$C_{10}H_7$—	68·63	69·07	4·32	4·40
p-$CH_3C_6H_4$—	60·48	60·96	5·44	5·76
o-$CH_3C_6H_4$—	60·48	60·25	5·44	5·41
p-$(CH_3)_2CH—C_6H_4$—	64·72	65·50	6·94	7·00
p-$C_6H_5—C_6H_4$—	71·64	72·20	4·76	4·78
γ-$C_6H_5—(CH_2)_3$—	64·72	63·40	6·94	7·15
β-$C_6H_5—C_2H_4$—	62·77	63·67	6·26	6·33
n-$C_4H_9OC_2H_4$—	48·32	48·32	9·06	9·05
Cyclo-C_6H_{11}—	55·01	55·59	8·85	8·87

* Corrected for water content.

TABLE 2.—PHYSICAL PROPERTIES OF SEVERAL ORGANOPHOSPHORIC ACIDS

Organophosphoric acid	Equivalent weight		Density 20°/20°	Index of refraction 25°	Viscosity (poises) 20°	Melting point (°C)	H_2O (%)
	Theory	Found					
Bis-(β-naphthyl)	350	349	1·336	—	—	142–143	nil
Bis-(p-tolyl)	278	278	1·285	—	—	81	0·18
Bis-(o-tolyl)	278	273	1·225	1·5434	13·573	—	0·76
Bis-(p-isopropylphenyl)	334	334	1·201	—	—	75	nil
Bis-(p-phenylphenyl)	402	402	1·169	—	—	240	nil
Bis-(γ-phenylpropyl)	334	332	1·156	1·5361	10·991	—	nil
Bis-(β-phenylethyl)	306	307	1·236	—	—	57–58	0·16
Bis-(n-butoxyethyl)	298	295	1·076	1·4391	0·863	—	0·89
Bis-(cyclohexyl)	262	261	1·156	—	—	77–79	0·19

DISCUSSION AND RESULTS

Cryoscopic measurements

The cryoscopic molecular weights indicate that in benzene the acids are dimeric, the behaviour being similar to that observed for other acids of this class.[1] In camphor, also, bis-(β-naphthyl)-phosphoric acid and bis-(p-tolyl)-phosphoric acid were found to be predominantly dimeric. However, bis-(p-tolyl)-phosphoric acid has been found to be monomeric in acetic acid.

Thus, even at 180°, the freezing point of camphor, the dimeric ring appears to be

stable; and only in the presence of a strong hydrogen bonding solvent, such as acetic acid, do these acids monomerize completely.

Infra-red absorption studies

Studies in the 3 μ region of 0·001 M carbon tetrachloride solutions of these acids in 4·5 mm cells showed no free OH absorption. In the 8–9 μ region a broad absorption continued to demonstrate a bonded phosphoryl group, even in 0·001 M carbon tetrachloride solutions (3 mm cells). These experiments are indicative that the association of the acids is strongly maintained even in dilute carbon tetrachloride solutions.

TABLE 3.—CRYOSCOPIC MOLECULAR WEIGHTS OF SEVERAL ORGANOPHOSPHORIC ACIDS

Organophosphoric acid	Cryoscopic solvent	Molality*	ΔT	Experimental molecular weight	Calculated molecular weight for dimer
Bis-(β-naphthyl)	Naphthalene insoluble in benzene and acetic acid	0·06	0·219	706	700
Bis-(*p*-tolyl)	Benzene	0·18	0·406	618	556
	Acetic acid	0·13	0·450	318	
Bis-(*o*-tolyl)	Benzene	0·28	0·683	574	556
Bis-(*p*-isopropylphenyl)	Benzene	0·08	0·196	703	668
Bis-(*p*-phenylphenyl)	Naphthalene and benzene insoluble				804
Bis-(γ-phenylpropyl)	Benzene	0·19	0·457	716	668
Bis-(β-phenylethyl)	Benzene	0·16	0·378	648	612
Bis-(n-butoxyethyl)	Benzene	0·14	0·367	599	596
Bis-(cyclohexyl)	Benzene	0·17	0·435	509	524

* Molality defined as (wt./formula wt.)/(1,000 g solvent).

(*a*) *Alkyl phosphoric acids.* The infra-red absorption frequencies for bis-(n-butoxyethyl)-phosphoric acid and bis-(cyclohexyl)-phosphoric acid from 650–4000 cm^{-1} are shown in Table 4. These acids give typical spectra for acids of the class $[(GO)GPO(OH)]_2$ or $[(GO)_2PO(OH)]_2$[1–4] where G is alkyl. The regions of interest in the spectra of the alkyl phosphoric acids have been previously discussed.[1] When G is cyclohexyl it is observed that the methylene CH scissor absorption shifts toward lower frequency (1455 cm^{-1}), and that ring vibrations are found in the 800–835 cm^{-1} region; which is characteristic of cyclohexyl compounds.[5]

(*b*) *Aryl phosphoric acids* (*Table 5 shows the absorption maxima*). These acids are discussed together because of the similarities in their infra-red spectra, and include bis-(phenyl),[1] bis-(*p*[1,1,3,3-tetramethylbutyl]phenyl),[3] bis-(β-naphthyl), bis-(*p*-phenylphenyl), bis-(*p*-isopropylphenyl), bis-(*p*-tolyl) and bis-(*o*-tolyl) phosphoric acids. Bis-(γ-phenylpropyl) and bis-(β-phenylethyl) phosphoric acids are also

[2] J. T. BRAUNHOLTZ, G. E. HALL, F. G. MANN and N. SHEPPARD, *J. Chem. Soc.* 868, (1959).
[4] L. C. THOMAS, *Chem. and Industr.* 197 (1957).
[4] D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **12**, 60 (1959).
[5] W. WEST, *Chemical Applications of Spectroscopy* p. 361. Interscience, New York (1956).

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discussed in this group, because they have the benzene ring in common with the aryl phosphoric acids. The spectra of these acids are considerably more complex than the alkyl phosphoric acids because of the ring associated vibrations. Nevertheless, characteristic absorptions due to the ring can be qualitatively identified and distinguished from those associated with the phosphorus atom. Complications will arise in regions where the absorption due to the ring and to the phosphorus atom overlap.

TABLE 4.—ABSORPTION MAXIMA IN CM^{-1} OF SEVERAL ALKYL PHOSPHORIC ACIDS

Bis-(cyclohexyl) phosphoric acid (KBr disk)	Bis-(butoxyethyl) phosphoric acid (Liquid film)
2930 (*s*)*	2950 (*s*)
2860 (*m*)	2910 (*s*)
2650 (*w*) broad	2860 (*s*)
2350 (*w*) broad	2650 (*m*) broad
1680 (*w*) broad	2300 (*m*) broad
1455 (*m*)	1680 (*m*) broad
1380 (*m*)	1460 (*m*)
1240 (*s*)	1380 (*m*)
1160 (*w*)	1365 (*m*)
1060 (*sh*)	1240 (*s*) broad
1035 (*vs*) broad	1130 (*vs*)
908 (*w*)	1050 (*vs*) broad
835 (*vw*)	900 (*m*)
800 (*vw*)	865 (*m*)
	825 (*m*)
	760 (*w*)
	670 (*w*)

* Abbreviations: *s*, strong; *m*, medium; *w*, weak; *v*, very; *sh*, shoulder.

Such a region is the phosphoryl oxygen region at about 1200–1250 cm^{-1}, but here formation of the sodium salt helps in making assignments. As was done for the alkyl phosphoric acids[1] the assignments made for the bonded P—OH absorptions were aided by salt or metallic complex formation, and by deuteration. It was observed that the spectra of the sodium salts sharpens up considerably, in contrast to the broad spectra of the acids.

Table 6 lists the absorptions tentatively assigned to the vibrations associated with the phosphorus atom portion of the molecule. Table 7 lists those absorptions tentatively assigned to the vibrations associated with the ring and/or ring substituent portion of the molecule.

(1) *Vibrations associated with the phosphorus atoms* (See Fig. 1). The spectra associated with the P atom are characteristic of dimeric monobasic acids (e.g. $[(GO)_2PO(OH)]_2$ or $[(GO)GPO(OH)]_2$)[1–4]. The broad regions associated with the bonded P—OH are observed at about 2250–2380 cm^{-1}, 2475–2700 cm^{-1} and 1700 cm^{-1} (Fig. 2). The phosphoryl stretching vibration occurs in the vicinity of about 1200 cm^{-1} and is difficult to determine because of several ring associated vibrations near this

TABLE 5.—ABSORPTION MAXIMA IN CM^{-1} OF SEVERAL ARYL–PHOSPHORIC ACIDS

bis-(phenyl) (KBr)	bis-(*p*-[1,1,3,3-tetramethyl-butyl]phenyl) (KBr)	bis-(*p*-tolyl) (KBr)	bis-(*o*-tolyl) (KBr)	bis-(β-naphthyl) (KBr)	bis-(β-phenylethyl) (KBr)	bis-(γ-phenyl-propyl) (Liquid film)	bis-(*p*-isopropyl) (KBr)	bis-(*p*-phenylphenyl) (KBr)
3100 (*w*)*	3120 (*w*)	3090 (*w*)	3100 (*w*)	3100 (*w*)	3080 (*w*)	3075 (*sh*)	3050 (*w*)	3060 (*s*)
	2980 (*s*)	2980 (*w*)	3000 (*sh*)		3050 (*w*)	3045 (*w*)		3040 (*w*)
	2925 (*sh*)	2900 (*sh*)	2970 (*w*)		3000 (*w*)	2965 (*m*), 2940 (*m*)	2960 (*m*)	
2550 (*m*) broad	2700 (*w*) broad	2800 (*w*)	2910 (*w*)		2985 (*w*)	2870 (*sh*)	2920 (*sh*)	
		2650 (*w*) broad	2700 (*w*) broad	2680 (*w*) broad	2700 (*w*) broad	2650 (*w*) broad	2870 (*w*)	
2380 (*m*) broad	2350 (*w*) broad	2475 (*w*) broad	2350 (*w*) broad	2250 (*w*)	2350 (*w*) broad	2300 (*w*) broad	2600 (*w*) broad	2490 (*w*) broad
2350 (*m*) broad					2150 (*m*) broad		2350 (*w*) broad	2290 (*w*) broad
	1890 (*w*)	1900 (*w*)		1690 (*sh*)				
1700 (*m*) broad	1700 (*w*) broad	1700 (*w*) broad	1700 (*w*) broad	1635 (*m*)	1700 (*m*) broad	1700 (*w*) broad	1670 (*w*) broad	1693 (*w*) broad
1590 (*m*)	1608 (*w*)	1610 (*m*)	1590 (*w*)	1600 (*m*)	1600 (*m*)	1610 (*w*)	1604 (*w*) broad	1606 (*m*)
1508 (*sh*)	1512 (*s*)	1510 (*s*) broad	1500 (*s*)	1518 (*m*)	1500 (*m*)	1502 (*m*)	1506 (*s*)	1524 (*m*)
1495 (*m*)	1480 (*m*)		1468 (*m*)					1495 (*s*)
	1450 (*sh*)			1470 (*m*)	1455 (*m*)	1460 (*m*)	1475 (*w*)	1479 (*w*)
	1410 (*sh*)							
	1398 (*w*)	1382 (*m*)	1385 (*w*)	1360 (*m*)	1380 (*sh*)		1376 (*w*)	1400 (*w*)
	1365 (*m*)	1310 (*m*)					1276 (*m*)	
1235 (*s*)	1265 (*s*)	1240 (*s*)	1260 (*sh*)	1245 (*s*)	1270 (*m*)	1230 (*m*) broad	1218 (*sh*)	1384 (*w*)
1215 (*s*)	1215 (*vs*)		1230 (*vs*)	1218 (*vs*)	1215 (*m*)			1344 (*w*)
1200 (*vs*)	1182 (*s*)	1195 (*vs*)	1178 (*vs*)	1165 (*vs*)			1200 (*vs*)	
1165 (*s*)	1130 (*w*)	1188 (*s*)	1115 (*vs*)	1145 (*s*)			1180 (*s*)	1229 (*s*) broad
		1165 (*s*)		1128 (*s*)	1090 (*sh*)			1200 (*s*)
1050 (*s*)	1095 (*w*)	1030 (*s*)	1050 (*sh*)	1010 (*vs*) broad	1070 (*s*)	1095 (*sh*)	1096 (*m*)	1172 (*s*)
1030 (*sh*)	1020 (*vs*)	1020 (*s*)	1030 (*vs*)		1050 (*s*)	1025 (*vs*)	1034 (*s*)	1114 (*w*)
1010 (*s*)					1025 (*s*)		1016 (*s*)	
970 (*vs*)	998 (*vs*)	990 (*vs*)	980 (*vs*)	988 (*sh*)	1008 (*s*)	990 (*sh*)	966 (*vs*)	1013 (*s*)
930 (*m*)	930 (*m*)	940 (*sh*)	940 (*sh*)	955 (*sh*)	940 (*m*)			1004 (*s*)
908 (*m*)				935 (*sh*)			921 (*m*)	
888 (*sh*)	835 (*s*)	830 (*s*)	818 (*m*)	895 (*s*)				992 (*s*)
		825 (*s*)	800 (*sh*)	870 (*s*)	820 (*w*)		834 (*s*)	847 (*s*)
				840 (*s*)	810 (*w*)			
778 (*m*)	790 (*w*)		765 (*s*)	830 (*sh*)			791 (*w*)	762 (*s*)
760 (*sh*)	770 (*w*)	725 (*m*)		755 (*m*)	755 (*m*)	745 (*m*)	766 (*w*)	
740 (*w*)	750 (*w*)			745 (*m*)			728 (*w*)	721 (*m*)
	730 (*w*)	700 (*m*)	715 (*w*)	712 (*m*)	705 (*m*)	695 (*m*)	685 (*w*)	
692 (*m*)	670 (*w*)		668 (*w*)			660 (*m*)	665 (*w*)	688 (*m*)

* Abbreviations: (*vs*), very strong; (*s*), strong; (*m*), medium; (*w*), weak; (*sh*), shoulder.

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TABLE 6.—ABSORPTION MAXIMA (ν, cm^{-1}) IN VARIOUS ARYL PHOSPHORIC ACIDS DUE TO VIBRATIONS ASSOCIATED WITH PHOSPHORUS ATOM (POSTULATED ASSIGNMENTS)

Dimer Phosphoric acid	Bonded P—OH Stretching*	Bonded P—OH Deformation	Bonded P→O Stretching	P—O—(G) Stretching asymmetric
bis-(phenyl)[1]	2550 (*m*) broad 2380 (*m*) broad 2350 (*m*) broad	1700 (*m*) broad	1200 (*vs*)	970 (*vs*)
bis-(*p*-[1,1,3,3-tetramethyl-butyl]phenyl)[1]	2700 (*w*) broad 2350 (*w*) broad	1700 (*w*) broad	1215 (*vs*)	998 (*vs*)
bis-(*p*-tolyl)	2650 (*w*) broad 2475 (*w*) broad	1700 (*w*) broad	1195 (*vs*)	990 (*vs*)
bis-(*o*-tolyl)	2700 (*w*) broad 2350 (*w*) broad	1700 (*w*) broad	1230 (*vs*)	980 (*vs*)
bis-(*β*-naphthyl)	2680 (*w*) broad 2250 (*w*)	1690 (*sh*)	1218 (*vs*)	1010 (*vs*) broad
bis-(*β*-phenylethyl)	2700 (*w*) broad 2350 (*w*) broad	1700 (*m*) broad	1215 (*m*)	1008 (*s*)
bis-(*γ*-phenylpropyl)	2650 (*w*) broad 2300 (*w*) broad	1700 (*w*) broad	1230 (*m*) broad	1025 (*vs*)
bis-(*p*-isopropylphenyl)	2600 (*w*) broad 2350 (*w*) broad	1680 (*w*) broad	1200 (*vs*)	966 (*vs*)
bis-(*p*-phenylphenyl)	2490 (*w*) broad 2290 (*w*) broad	1693 (*w*) broad	1200 (*s*)	992 (*s*)

* The lower frequency in this column has been assigned by THOMAS[3] as being due to the overtone of the P—O stretching vibration.

TABLE 7.—ABSORPTION MAXIMA (ν, cm^{-1}) IN VARIOUS ARYL PHOSPHORIC ACIDS DUE TO VIBRATIONS ASSOCIATED WITH RING AND/OR RING SUBSTITUENTS (POSTULATED ASSIGNMENTS)

Phosphoric acid	C—H stretching		C—C skeletal in-plane	C—H deformation	(P)—O—G stretching
	Ring	Methyl, Methylene			
bis-(phenyl)[1]	3100 (*w*)	—	1590 (*m*), 1508 (*sh*) 1495 (*m*)	—	1165 (*s*)
bis-(*p*-[1,1,3,3-tetramethyl-butyl]phenyl)[1]	3120 (*w*)	2980 (*s*), 2925 (*sh*)	1608 (*w*), 1512 (*s*)	1480 (*m*), 1450 (*sh*), 1410 (*sh*), 1398 (*w*), 1365 (*m*)	1182 (*s*)
bis-(*p*-tolyl)	3090 (*w*)	2980 (*w*), 2900 (*sh*), 2800 (*w*)	1610 (*m*), 1510 (*s*) broad	1382 (*m*)	1188 (*s*) 1165 (*s*)
bis-(*o*-tolyl)	3100 (*w*)	3000 (*sh*), 2970 (*w*), 2910 (*w*)	1590 (*w*), 1500 (*s*)	1468 (*m*), 1385 (*w*)	1178 (*vs*)
bis-(*β*-naphthyl)	3100 (*w*)	—	1600 (*m*), 1518 (*m*)	—	1165 (*vs*)
bis-(*β*-phenylethyl)	3080 (*w*) 3050 (*w*)	3000 (*w*), 2985 (*w*)	1600 (*m*), 1500 (*m*)	1455 (*m*), 1380 (*sh*)	—
bis-(*γ*-phenylpropyl)	3075 (*sh*) 3045 (*w*)	2965 (*m*), 2940 (*m*), 2870 (*sh*)	1610 (*w*), 1502 (*m*)	1460 (*m*)	—
bis-(*p*-isopropylphenyl)	3050 (*w*)	2960 (*w*), 2920 (*sh*), 2870 (*w*)	1604 (*w*), 1506 (*s*)	1475 (*w*), 1376 (*w*)	1180 (*s*)
bis-(*p*-phenylphenyl)	3060 (*sh*) 3040 (*w*)	—	1606 (*m*), 1495 (*s*)	—	1172 (*s*)

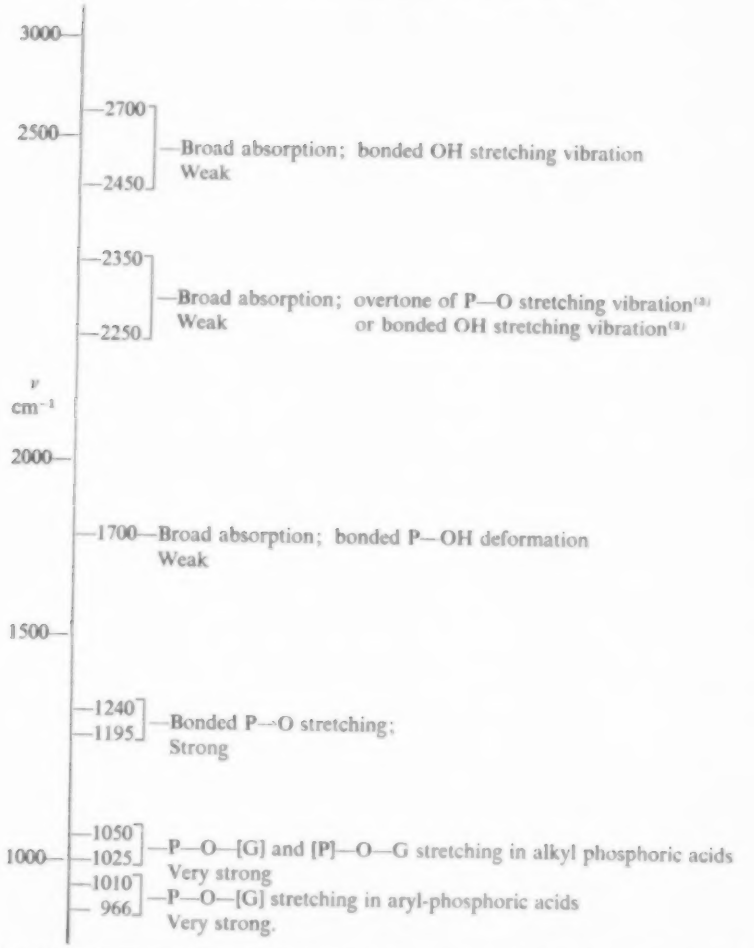
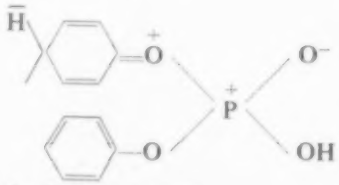


FIG. 1.—Schematic diagram illustrating the vibrations associated with phosphorus atom in alkyl and aryl phosphoric acids (postulated assignments).

region (Fig. 3). However, preparation of the sodium salts aided in selecting the vibration due to the P → O group. The position of the P → O vibrations appear at 1195–1230 cm^{-1}, and there is a tendency for a shift toward lower frequency to occur as the G group becomes aryl. A similar behaviour of the carbonyl frequency has been observed with the benzoic acids.[6] Because of the strong electronegative nature of the phenyl and substituted phenyl groups high contribution from the resonating structure



[6] M. ST. C. FLETT, *Trans. Faraday Soc.* **44**, 767 (1948).

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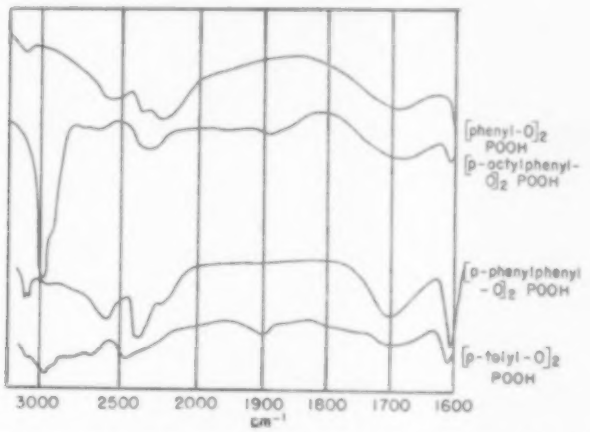

FIG. 2.—Absorption frequencies in the region of 1600–3000 cm^{-1} for several aryl phosphoric acids (P—OH stretching and deformation, and C—H stretching vibrations). KBr disks.

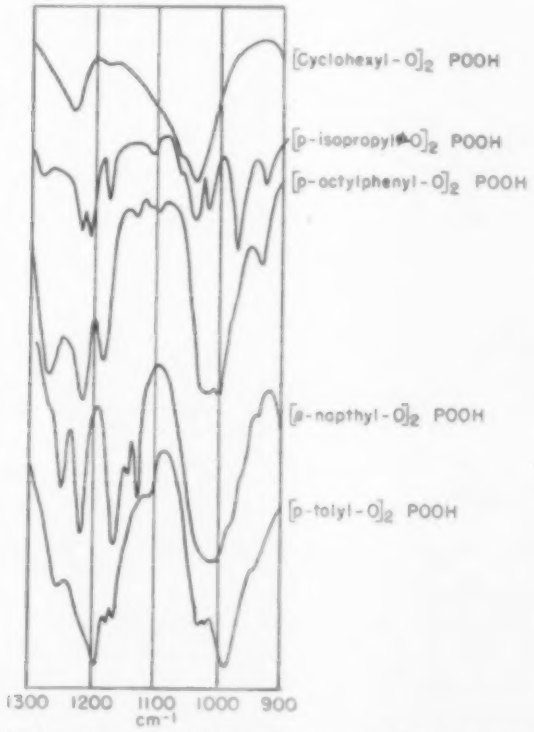

FIG. 3.—Absorption frequencies in region of 900–1300 cm^{-1} (bonded P→O stretching, P—O—(G) stretching (asymmetric), (P)—O—G stretching, vibrations). KBr disks.

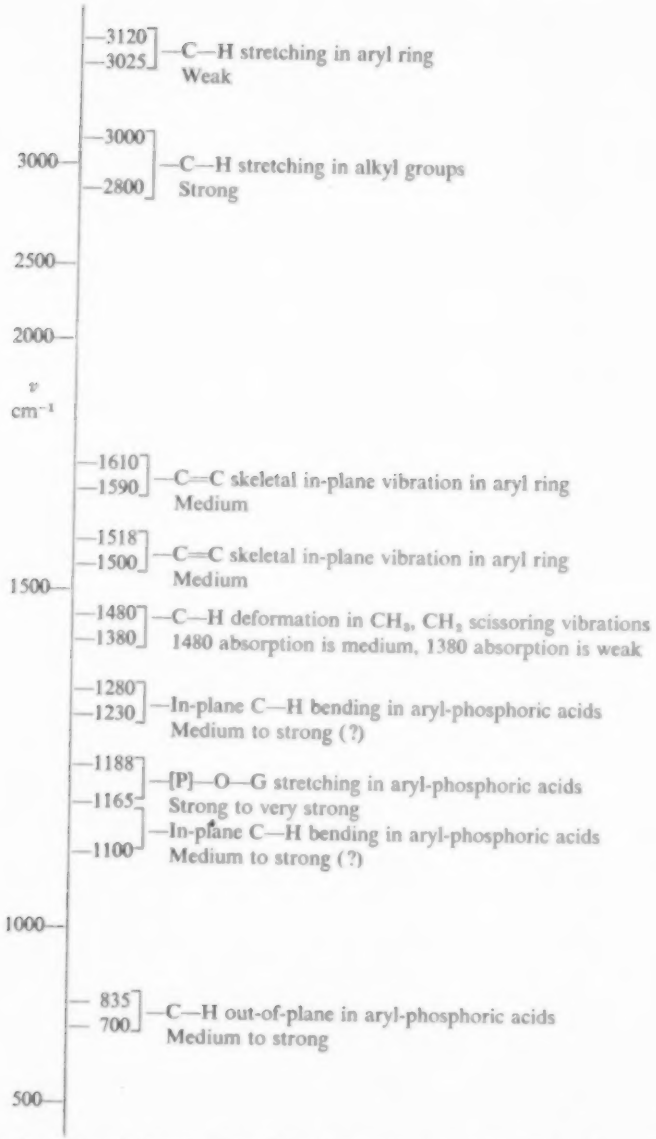

FIG. 4.—Schematic diagram illustrating the vibrations associated with the benzene ring and/or ring substituent in aryl-phosphoric acids (postulated assignment).

is possible, which weakens both the phosphoryl and the P—O—(G) bonds and shifts them to lower frequencies. The P—O—(Φ) stretching vibration (asymmetric) appears as a very strong band at about 966–1010 cm^{-1}, confirming the assignment of NYQUIST and MORTIMER[7,8] for this absorption, and is at a lower frequency than for alkyl phosphoric acids. The location of this frequency is also aided by sodium salt

[7] R. A. NYQUIST, *Appl. Spectroscopy* No. 4, 161 (1957).
[8] F. S. MORTIMER, *Spectrochim. Acta* **9**, 270 (1957).

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formation, since the absorption appears to shift to lower frequency on salt formation.[9] The corresponding symmetric vibration is difficult to identify because several peaks occur in the region of the out-of-plane hydrogen vibrations (700–835 cm^{-1}).

(2) *Vibrations associated with the ring or ring substituents in aryl phosphoric acids.* The CH stretching, CH bending and ring skeletal (see Fig. 2, 4) vibrations can be very readily located. These appear to give the typical spectra for ring or ring substituent compounds in the 2800–3100 cm^{-1} region (Fig. 2) and at 1600 cm^{-1} and

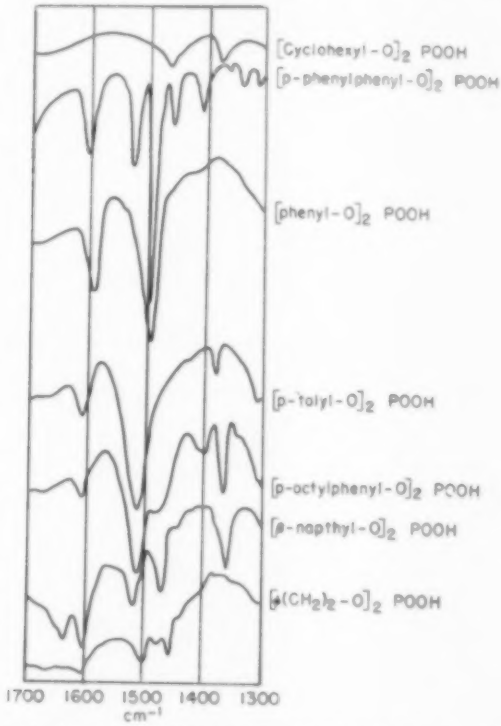

FIG. 5.—Absorption frequencies in the region of 1300–1700 cm^{-1} for several aryl phosphoric acids (C=C skeletal in-plane and C—H deformation vibrations). KBr disks.

1500 cm^{-1} (Fig. 5.) The 1500 cm^{-1} band usually is stronger than the 1600 cm^{-1} band in these compounds. The CH_3 degenerate deformation bands for the alkyl substituents on the ring are readily identified in the region 1365–1480 cm^{-1} (Fig. 5). It is much more difficult to assign the CH in-plane and out-of-plane vibrations. RANDLE and WHIFFEN[10] have attributed absorption in the 1000–1170 cm^{-1} region to in-plane hydrogen bending motions in aryl hydrocarbons. The aryl phosphoric acids do have some strong absorptions in the 1050 cm^{-1} and 1100–1165 cm^{-1} regions and these can possibly be partly due to the in-plane hydrogen bending vibrations. Bis-(β-phenylethyl)-phosphoric acid for example, has strong absorption in the 1000–1100 cm^{-1} region. In addition to the P—O—(G) asymmetric stretching vibration at 1000 cm^{-1},

[9] J. R. FERRARO. Unpublished work (1960).
[10] H. M. RANDLE and D. H. WHIFFEN, *Molecular Spectroscopy*; Report on the conference held in London by the Institute of Petroleum (Oct. 1954).

in-plane hydrogen vibrations may occur here. Actually in the region from 1008–1070 cm^{-1} there are four strong bands for this acid.

The out-of-plane hydrogen motions for these acids are found in the region 700–835 cm^{-1} (Fig. 6), and several absorption maxima appear in this region. The 1,4 disubstituted phenylphosphoric acids show maximum absorptions at higher frequency ($>800\ cm^{-1}$) than the monosubstituted or the 1,2 disubstituted acids. This is the expected behaviour[5,10,11,12] for substituted phenyl compounds.

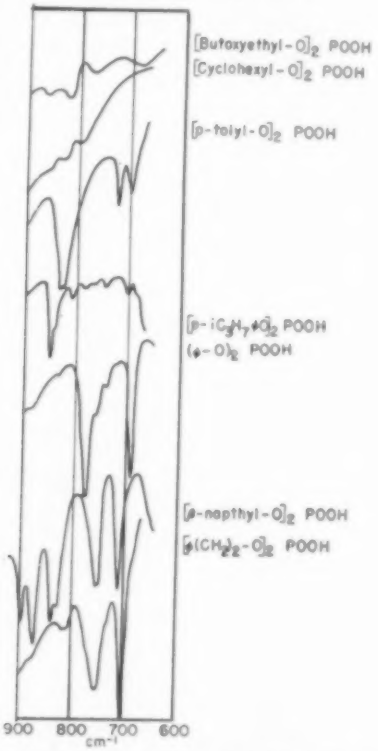

FIG. 6.—Absorption frequencies in the region of 600–900 cm^{-1} (out-of-plane hydrogen vibrations) KBr disks.

All the aryl acids show a strong absorption at about 1180 cm^{-1}, and this is attributed to (P)—O—Φ stretch in organophosphoric compounds[7,8] containing the O—Φ link. This absorption is absent in monobasic alkyl phosphoric acids, and in bis-(β-phenylethyl) and bis-(γ-phenylpropyl)-phosphoric acids because of absence of a O—Φ group.

Absorptions at 1230–1280 cm^{-1}, usually strong in these acids are not assigned. MORTIMER[8] assigns these in $(\Phi O)_3P \rightarrow O$ to in-plane bending modes of hydrogen.

[11] J. L. HAWKINS, E. R. WARD and D. H. WHIFFEN, *Spectrochim. Acta* **10**, 105 (1957).
[12] L. J. BELLAMY, *The Infrared Spectra of Complex Molecules*. John Wiley, New York (1958).

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J. Inorg. Nucl. Chem., 1961, Vol. 16, pp. 257 to 259. Pergamon Press Ltd. Printed in Northern Ireland

ADDITION COMPOUNDS OF CHROMIUM(VI) OXIDE WITH HETEROCYCLIC NITROGEN BASES—III

REACTIONS WITH QUINALDINE, ACRIDINE, 1,10-PHENANTHROLINE AND TRIBENZYLAMINE

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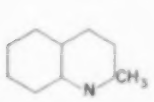
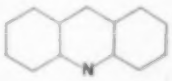
(*Received* 20 *June* 1960)

PREVIOUS work[1,2] in this laboratory has shown that unhindered heterocyclic nitrogen bases, such as pyridine, β- and α-picoline, some of the lutidines and quinoline, readily form with chromium(VI) oxide addition compounds corresponding to the formula $CrO_3 \cdot 2B$ (B = one molecule of nitrogen base) when the chromium oxide is added to the anhydrous amine at or near room temperature. On the other hand, α-picoline and lutidines having a methyl group in the 2-position have been shown to undergo considerable oxidation by chromium(VI) oxide under these conditions, and highly hindered bases such as 2,4,6-collidine and 2,6-lutidine do not react with chromium(VI) oxide under the conditions of these studies.

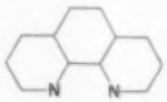
At lower temperatures (ca. $-60°$), however, α-picoline forms without appreciable oxidation a well-defined 1 : 1 adduct corresponding to the formula $CrO_3 \cdot B$.[2] We were interested in determining whether this same distinctive behaviour toward chromium(VI) oxide obtains with other heterocyclic nitrogen bases with a similar degree of steric hindrance. Therefore, the reactions of chromium(VI) oxide with bases having the following structural formulae were studied:



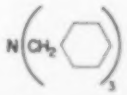
Quinaldine



Acridine



1,10-phenanthroline



Tribenzylamine

EXPERIMENTAL

Materials. Quinaldine obtained from the Matheson Co. Inc. was dried with barium oxide and fractionated under reduced pressure through a 4ft column packed with glass helices. The purity was checked by boiling point and refractive index both of which agreed with recorded values. (b.p. 118° at 10 mm; $n_D^{25°} = 1{\cdot}6072$; lit. $n_D^{20°} = 1{\cdot}6091$) Acridine obtained from Fisher Scientific Co. was purified by recrystallization from ether (m.p. 108–9°; lit. 110°). Hydrated 1,10-phenanthroline obtained from the G. F. SMITH Chemical Co. was dehydrated over phosphorus(V) oxide under vacuum. The anhydrous product melted at 116° (lit. 117°). Tribenzylamine from Eastman Kodak Co. was recrystallized from ethanol. (m.p. 91°; lit. 92°). Chromium(VI) oxide (Mallinckrodt C.P. grade) was dried at 140° at 0·1 mm Hg pressure over phosphorus(V) oxide for 48 hr. It was then finely ground and dried an additional 48 hr under the same conditions and stored over phosphorus(V) oxide.

* Present address: Dept. of Chemistry, University of Florida, Gainesville, Florida.

[1] H. H. SISLER, J. D. BUSH and O. E ACCOUNTIUS, *J. Amer. Chem. Soc.* **70**, 3827 (1948).
[2] H. H. SISLER, W. C. L. MING, E. METTER, and F. R. HURLEY, *J. Amer. Chem. Soc.* **75**, 446 (1953).

Procedure. Previous studies in this series had followed the procedure of dissolving the chromium (VI) oxide in an excess of amine and then evaporating the excess amine under reduced pressure. This procedure was unsatisfactory for solid amines and also for quinaldine because of the low rate of solution of chromium(VI) oxide in the amine at room temperature and also because of the very slow rate of evaporation of the excess amine at room temperature or below, even under very low pressures. Therefore, the following procedure was adopted:

About 25 ml of very dry acetone (C.P. grade) was placed in a closed centrifuge tube and cooled to −80°. This acetone was added to a small, weighed sample of chromium(VI) oxide in another precooled centrifuge tube. This closed tube was then continuously shaken at −80° until complete solution had occurred. Requisite amounts of the amine (corresponding to amine/CrO_3 ratios of from 2:1 to 0·6:1) were dissolved in 10 ml portions of precooled acetone and were added to the chromium(VI) oxide solution and the reaction mixture shaken until reaction appeared to be complete (evidenced by change in colour). During the reaction (reaction time varied from a few minutes to several hours) the mixture was kept cold (−80°) and was protected from light. The solid was separated from the mother liquor by centrifugation, was washed several times with precooled acetone and dried under reduced pressure. Accurate yield data were not obtained since some of the product was lost in the decantate and some of the addition compounds are slightly soluble in acetone; however, the yields appear to be essentially quantitative. The products were removed from the reaction vessel in a dry box and stored in tightly closed containers protected from the light. The methods for analysis of the products for Cr(VI) and Cr(III) are essentially those reported in the first paper in this series.[1]

Reaction of chromium(VI) *oxide with quinaldine.* When solutions of chromium(VI) oxide and quinaldine in acetone at −80° were mixed a bright yellow solid appeared. Isolation of this solid yielded a yellow powder which contained less than 0·5% Cr(III) and which melted at 125–8° but which darkened at 118°. Several typical products gave the following analyses. (Found; Cr, 19·96 21·35, 20·94. Calc. for $CrO_3 \cdot C_{10}H_9N$: Cr, 21·38. Calc. for $CrO_3 \cdot 2C_{10}H_9N$: Cr, 11·97%.) Direct exposure to light and moisture causes the product to change from yellow to brown in a few minutes. However, some of the product was stored in a dry box protected against light for eight months with no apparent colour change.

Reaction of chromium(VI) *oxide with acridine.* The reaction of acridine with chromium(VI) oxide at −80° in acetone solution immediately yielded a yellow product plus a very small amount of brownish-green material which adhered to the bottom of the tube. The yellow product, contaminated with only a trace of the brown impurity was analysed and was found to contain only from 0·3 to 0·7% Cr(III). Analytical data on several typical samples corresponding to different mole ratios of reactants are as follows. (Found; Cr, 18·30, 19·20, 18·94. Calc. for $CrO_3 \cdot C_{13}H_9N$: Cr, 18·78%. Calc. for $CrO_3 \cdot 2C_{13}H_9N$: Cr, 11·35%.) The addition compound begins to decompose at 194–5°C and is much less sensitive to light than the other addition compounds reported in this study.

Reaction of chromium(VI) *oxide with* 1,10-*phenanthroline.* The reaction of 1,10-phenanthroline with chromium(VI) oxide in acetone solution at −80° takes place at a somewhat slower rate than the corresponding reactions with quinaldine and acridine. The yellow product obtained in this reaction contained from 0·4 to 1·0% Cr(III) but the analytical data for reactions at various amine to CrO_3 ratios indicated that the product was essentially $CrO_3 \cdot C_{12}H_8N_2$. (Found: Cr, 15·85, 17·49, 17·54, 18·25. Calc. for $CrO_3 \cdot C_{12}H_8N_2$; Cr, 18·5. Calc. for $CrO_3 \cdot 2C_{12}H_8N_2$, Cr, 11·07%.) The yellow addition compound is slightly soluble in acetone and ether. It begins to decompose in the range of 115°–120°.

Reaction of chromium(VI) *oxide with tribenzylamine.* When acetone solutions of chromium(VI) oxide and tribenzylamine are mixed at −80° the solution takes on a yellow-orange tint. On standing without stirring for approximately 24 hr a precipitate of granular orange crystals formed. These crystals melted at 64°. In a series of experiments carried out in this manner, there was in no case more than 0·2% Cr(III) in the product. Analysis of a series of products. (Found: Cr, 11·53, 11·85, 11·60. Calc. for $CrO_3 \cdot C_{21}H_{21}N$: Cr, 13·42%.) The infra-red spectrum of the addition compound was taken and gave adsorption bands characteristic of acetone. The %Cr calculated for the complex $CrO_3 \cdot C_{21}H_{21}N \cdot (CH_3)_2C{=}O$ is 11·67 which agrees well with the analytical data obtained.

After these results were obtained the reaction of chromium(VI) oxide with tribenzylamine was carried out as follows: After the acetone solutions of the two reactants were mixed at −80° the mixture was shaken every 2 or 3 min. After about 3 hr a yellow, finely divided solid had formed. This solid was isolated by centrifugation. It melted at 112°. This yellow solid contained very small

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amounts of the orange crystals obtained by the other procedure. The yellow product is soluble in acetone and ethyl alcohol, but is insoluble in ether. Analysis of the yellow solid from a series of these experiments at varying mole ratios showed the presence of from 0·2 to 0·4% Cr(III). Analyses for Cr(VI) for this series are as follows. (Found: Cr, 13·37, 12·70, 12·54. Calc. for $CrO_3 \cdot C_{21}H_{21}N$: Cr, 13·42. Calc. for $CrO_3 \cdot 2C_{21}H_{21}N$: Cr, 7·20%.) To further elucidate the relation between the orange and yellow products, a sample of the orange crystals was finely ground and placed under reduced pressure at room temperature overnight. The colour changed to yellow and the infra-red spectrum contained no acetone bands. It appears, therefore, that the immediate product of the chromium(VI) oxide–tribenzylamine reaction is yellow $CrO_3 \cdot (C_6H_5CH_2)_3N$ but that on standing in the acetone solution (or suspension) the yellow adduct is slowly converted to orange crystals of $CrO_3 \cdot (C_6H_5CH_2)_3N \cdot (CH_3)_2CO$.

DISCUSSION

The results of the study of the reactions of chromium(VI) oxide with quinaldine, acridine, 1,10-phenanthroline and tribenzylamine have shown that these substances behave in a manner analogous to that of α-picoline[2] in that all four of these amines form 1 : 1 addition compounds with chromium(VI) oxide provided that the reactions are carried out at low temperature. If it is accepted that the factor which determines the formula of these addition compounds is steric then we may assume that steric interference about the nitrogen atom in quinaldine, acridine and tribenzylamine is of the same order as that in α-picoline and is intermediate between that in 2,6-lutidine and 2,4,6-collidine which do not form addition compounds with chromium(VI) oxide and that of pyridine, β-picoline, γ-picoline, and quinoline which readily form compounds of the formula $CrO_3 \cdot 2B$.

In the case of 1,10-phenanthroline we cannot be sure that the 1 : 1 adduct obtained is really analogous to the other 1 : 1 addition compounds; for there is a distinct possibility that both nitrogen atoms of the phenanthroline are co-ordinated with the chromium atom. From the structure of 1,10-phenanthroline and its usual behaviour on co-ordination, bidentate chelation is highly probable. This is in accord with the tentative suggestion in an earler paper[2] that adducts of the general formula $CrO_3 \cdot 2B$ contain 5-covalent chromium.

One may view the reactions of chromium(VI) oxide with nitrogen bases as involving, as a first stage, the formation of the 1 : 1 adduct. This process requires the conversion of the octahedral chromium in the solid CrO_3 to a tetrahedral configuration in analogy to the hydration of CrO_3 to chromic acid. In those instances where further co-ordination is not restricted by steric or other factors the 1 : 1 adduct may be converted to the product $CrO_3 \cdot 2B$ in which it is probable that the co-ordination number of chromium is increased from four to five.

The formation of the stoicheiometric acetone solvate, $CrO_3 \cdot (C_6H_5CH_2)_3N \cdot (CH_3)_2CO$, in the reaction of chromium(VI) oxide with tribenzylamine may be interpreted in similar terms. The relative steric requirements of acetone and tribenzylamine may permit the acetone to add to the chromium during the second stage of the reaction. If the acetone actually is co-ordinated, the binding must be relatively weak as evidenced by the ease of its removal under vacuum and by the occurrence of the $\rangle C{=}O$ stretching frequency essentially unaltered in the infra-red spectrum of the solvated addition compound.

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TETRAVALENT LANTHANIDES—I

SODIUM PRASEODYMIUM(IV) FLUORIDES*†

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(*Received* 29 *February* 1960)

Abstract—The compounds $NaPrF_5$ and Na_2PrF_6 containing tetravalent praseodymium have been prepared by oxidation of the chlorides with elemental fluorine at elevated temperatures. The compounds were identified by X-ray diffraction methods. Further proof of the tetravalency of the praseodymium was obtained by absorption spectrophotometry and by iodometry.

OF the fifteen lanthanide elements, only cerium, praseodymium, and terbium form compounds in which the lanthanide is in the plus four oxidation state. The dioxides of these elements have all been prepared.[1,2,3] The tetrafluorides of cerium and terbium also have been prepared,[4,5] but similar attempts to prepare PrF_4 were unsuccessful[5,6,7] except in solid solutions with cerium tetrafluoride.[8]

In a long series of papers, Professor WILHELM KLEMM and his colleagues[9] have reported the preparation of compounds containing an alkali metal, fluorine, and a transition metal where the transition metal has an oxidation state much higher than usual, i.e. K_3NiF_6 and K_2NiF_6. It was felt that such an approach might yield a stable compound containing Pr(IV). The compound $KPrF_5$ has been reported but has not been completely characterized.[10]

After the completion of this work HOPPE[11] reported in a note the preparation of alkali metal-praseodymium(IV) fluorides where the ratio of alkali metal to praseodymium was two. Few data are given in HOPPE's brief note although X-ray studies, magnetic susceptibility, and iodide ion oxidation were used to prove the tetravalency of praseodymium in these compounds.

In this paper, a study of the sodium–praseodymium fluoride system is reported where the sodium to praseodymium ratios are 1:1, 2:1 and 4:1.

EXPERIMENTAL

The rare earth oxides used in this study were 99·9 per cent pure. All other chemicals were of reagent grade and were used without further purification. The fluorine gas was obtained from

* Work done under the authority of the U.S. Atomic Energy Commission.
† Presented in part before the XVIIth International Congress of Pure and Applied Chemistry, 1959.

(1) V. M. GOLDSCHMIDT, F. ULRICH and T. F. W. BARTH, *Osloer. Akad. Ber.* 5 (1925).
(2) F. SCHERRER and J. PALACIOS, *Anal. Fis. Quim.* **26**, 309 (1928).
(3) D. M. GRUEN, W. C. KOEHLER and J. J. KATZ, *J. Amer. Chem. Soc.* **73**, 1475 (1951).
(4) W. KLEMM and P. HENKEL, *Z. Anorg. Chem.* **220**, 180 (1934).
(5) B. B. CUNNINGHAM, D. C. FEAY and M. G. ROLLIER, *J. Amer. Chem. Soc.* **76**, 3361 (1954).
(6) A. I. POPOV and G. GLOCKLER, *J. Amer. Chem. Soc.* **74**, 1357 (1952).
(7) T. PERROS and C. R. NAESER, *J. Amer. Chem. Soc.* **74**, 3694 (1952).
(8) W. P. BRYAN, UCRL-3894 (Thesis), University of California, Berkeley, Calif. (1957).
(9) For a review, see W. KLEMM, *Angew. Chem.* **63**, 396 (1951); and W. KLEMM, *Anorganische Chemie* (9th Ed.). W. de Gruyter, Berlin (1956).
(10) T. PERROS, NYO-7597 (1956).
(11) R. HOPPE, *Angew. Chem.* **71**, 457 (1959).

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pressurized cylinders and passed through a sodium fluoride-potassium fluoride trap to remove HF. The fluorinator has been described previously.[12]

Standard solutions of the rare earths were prepared by dissolving weighed amounts of the oxide in hydrochloric acid. Alkali metal chloride standard solutions were also prepared. Aliquots of these solutions were then mixed to prepare different stoicheiometric ratios of alkali metal to lanthanide These chloride solutions were heated and evaporated to dryness in air in a mullite mortar and then ground to a fine powder. This powder was placed in a well in an optical quality calcium fluoride disk. Fluorination of the mixture was then carried out in a nickel fluorinator at temperatures from 200° to 400°C over a period of hours. After displacement of fluorine gas from the fluorinator by helium, the samples were removed and quickly capped by a thin, fused-silica disk, using a fluorocarbon grease to insure a seal between the calcium fluoride holder and the silica disk. Such a mounting protected the product from the atmosphere and allowed it to be examined in the model 14 Cary Spectrophotometer. The technique used for spectral determinations has been described in connexion with similar studies on the tetrafluorides of americium and curium.[13]

An inert atmosphere drybox was used for preparation of X-ray samples. A conventional thin-walled capillary was employed to mount the samples and showed no evidence of attack over a period of many hours. The patterns were obtained by means of a 114·6 mm diameter camera with Eastman Type A or AA film using filtered copper radiation.

An iodometric method was developed using CeF_4 as a standard material. Aluminium chloride was added to the iodide solution to aid in the dissolution of the fluoride. Pure CeF_4 was added to a solution 1 M in KI, 1 M in HCl, and 1 M in $AlCl_3$, and the solution was stirred for 1 hr in an argon atmosphere. Consistent values corresponding to 97–98 per cent Ce(IV) were obtained upon titration of the liberated iodine by standard thiosulphate. This same technique was used for analysis of the praseodymium samples.

RESULTS AND DISCUSSION

Visual observation showed that the fluorinated products were white in comparison with the pale green starting materials. In Table 1 the analytical data are given for the oxidized compounds.

TABLE 1.—EVIDENCE FOR THE EXISTENCE OF TETRAVALENT PRASEODYMIUM

Na/Pr	Absorption spectra	Iodometric analysis	X-Ray diffraction data
1:1	weak Pr(III) lines >85% Pr(IV)	>75% Pr(IV)	$NaPrF_5$, rhombohedral, $a = 8{\cdot}96 \pm 0{\cdot}02$ Å $\alpha = 107{\cdot}9 \pm 0{\cdot}2°$
2:1	very weak Pr(III) lines, >95% Pr(IV)	≧97% Pr(IV)	Na_2PrF_6, orthorhombic, $a = 5{\cdot}54 \pm 0{\cdot}02$ Å $b = 3{\cdot}97 \pm 0{\cdot}02$ Å $c = 11{\cdot}57 \pm 0{\cdot}06$ Å
4:1	very weak Pr(III) lines, >95% Pr(IV)	≧97% Pr(IV)	good diffraction pattern, not identified

The absorption spectra values were based on the relative absence of the Pr(III) maxima in the oxidized compound compared to the strong absorption reappearing after hydrogen reduction. The low value of about 85 per cent Pr(IV) for the 1:1 compound could be due to rapid attack by the atmosphere during transfer of the sample, since it was observed that this 1:1 compound was considerably less stable than the other two. No distinct structure was observed for the oxidized species over the range 2500–20,000 Å, although increased ultra-violet absorption was noted. Since Pr(IV) is isoelectronic with Ce(III), the absence of absorption in the visible and

[12] L. B. ASPREY, *J. Amer. Chem. Soc.* **76**, 2019 (1954).
[13] L. B. ASPREY and T. K. KEENAN, *J. Inorg. Nucl. Chem.* **7**, 27 (1958).

near infra-red is not surprising. In the ultra-violet, due to the increased light scattering by the crystals, the weaker intensity of the light source and the greater general absorption by the compounds in the ultra-violet, it is possible that weak narrow peaks may exist, although none were found.

Iodometric analysis of the compound containing a 1:1 ratio of sodium to praseodymium gave variable results, the highest corresponding to 76 per cent Pr(IV). It was observed that this compound dissolved much more rapidly than the others with a considerable evolution of gas. It seems probable that the low value of the oxidation number obtained was due to the rapid oxidation of water by the Pr(IV).

X-Ray powder patterns were obtained for the three compounds, and for the products of their reduction. In the case of the sodium to praseodymium ratio of 1:1, a rhombohedral structure was found, isostructural with $NaUF_5$.[14] The pattern of this same material after hydrogen reduction at 400°C showed it to be primarily hexagonal* $NaPrF_4$ with $a = 6{\cdot}11 \pm 0{\cdot}01$ Å and $c = 3{\cdot}74 \pm 0{\cdot}01$ Å, isostructural with $NaPuF_4$.[14] The compound with a sodium to praseodymium ratio of 2:1 was identified as being γ-Na_2PrF_6, isostructural with orthorhombic γ-Na_2UF_6.[14] The reduction product was composed of $NaPrF_4$ and NaF. The compound with a sodium to praseodymium ratio of 4:1 could not be identified but showed $NaPrF_4$ and NaF to be present after reduction, with more NaF than in the 2:1 case.

OTHER TETRAVALENT RARE EARTHS

Some evidence has been obtained for the existence of tetravalent neodymium and dysprosium in complex fluorides with the heavy alkali metals, rubidium and cesium. Further work is being carried out on these compounds in collaboration with R. HOPPE and W. KLEMM at the University of Münster.

Acknowledgements—Thanks are especially due to Professor JOHN C. BAILAR, JR., who originally called our attention to the work of KLEMM *et al.* We wish also to thank F. H. ELLINGER of this Laboratory for the preparation and interpretation of the X-ray powder patterns.

[14] W. H. ZACHARIASEN, *J. Amer. Chem. Soc.* **70**, 2147 (1948).

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REFLECTANCE SPECTRA OF PRASEODYMIUM OXIDES IN THE COMPOSITION RANGE Pr_2O_3 TO Pr_6O_{11}*

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(*Received* 8 *June* 1960)

Abstract—The spectra of praseodymium oxides (PrO_x) has been studied in the composition range $1{\cdot}5 \leq x \leq 1{\cdot}83$ from 200 to 2000 mμ. An ultra-violet cut-off was observed at about 320 mμ. Electronic transitions associated with the praseodymium ion are observed in the spectral range 400–650 mμ, and a band observed in the near infra-red which begins at 900 mμ.

THE reflectance spectra of various praseodymium oxides have been measured as a part of a study on the oxidation chemistry of this oxide system.

This material has been previously studied by EPHRAIM and BLOCK[1], who obtained the spectra of Pr_2O_3 in the visible region of the spectra. This oxide was also studied cursorily by MAZZA and JANELLI[2] and BOULANGER[3]. The oxide $PrO_{1{\cdot}83}$ has been investigated by HASS *et al.*[4]

In the present study an attempt is made to obtain information on the oxides PrO_x in the composition range $1{\cdot}50 \leq x \leq 1{\cdot}83$. It is known that the electrical properties undergo a rather marked change as the composition is altered from $PrO_{1{\cdot}5}$ to $PrO_{1{\cdot}83}$. The conductivity is markedly changed,[5] and the thermo-electric properties greatly effected.[6] Because of the immediate relation between electrical and optical properties[7] and the need of information in this regard it was felt desirable to obtain data on the spectra of PrO_x.

EXPERIMENTAL

The material used for this study was obtained from F. H. Spedding, Iowa State College, and The Lindsay Chemical Company and had a purity of greater than 99·9%. The non-stoicheiometric compositions were prepared by heating under vacuum conditions, or under controlled oxygen pressure at a series of definite temperatures. The samples were then analysed for oxygen in excess of the $PrO_{1{\cdot}5}$ composition by means of vacuum technique previously described.[8] The compositions indicated are accurate to about 0·003 stoicheiometric units.

The powdered samples were pressed into aluminium planchets, and the spectra observed by means of a Beckman DU spectrophotometer and reflection attachment.§ The intensities were referred to magnesium carbonate U.S.P. as a reference standard; a photomultiplier tube was used in the

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‡ Present address: Lincoln Lab., Lexington, Mass.

§ The authors wish to thank Dr. R. B. FISCHER for the loan of the latter equipment.

[1] F. EPHRAIM and R. BLOCK, *Ber. Dtsch. Chem. Ges.* **61**, B 80 (1938).
[2] L. MAZZA and A. JANELLI, *Atti Accad. Linncei* **7**, 44 (1951).
[3] F. BOULANGER, *C. R. Acad. Sci., Paris* **233**, 650 (1951).
[4] G. HASS, J. B. RAMSEY, A. THUN, *J. Opt. Soc. Amer.* **49**, 116 (1959).
[5] M. FOEX, *C. R. Acad. Sci., Paris* **220**, 359 (1945).
[6a] R. L. MARTIN, *Nature, Lond.* **165**, 202 (1950); [b] Quarterly Progress Report, Solid State Research, Lincoln Lab., Massachusetts Inst. of Tech., Jan. 1960, July 1959.
[7a] A. H. WILSON, *Theory of Metals*. Cambridge University Press (1960); [b] F. SETZ, *Modern Theory of Solids*. McGraw-Hill, New York (1940).
[8] F. VRATNY *Anal. Chim. Acta* **21**, 579 (1959).

visible region. The measurement techniques have been previously described by one of the authors.[9] From previous experience and results reported from the National Bureau of Standards[10] it is felt that the reflectance intensities are accurate to about 1 per cent.

RESULTS

The reflectance spectra are reproduced in Figs. 1–3. From these figures it may be seen that in general PrO_x has a low reflectance in the ultra-violet and near infra-red

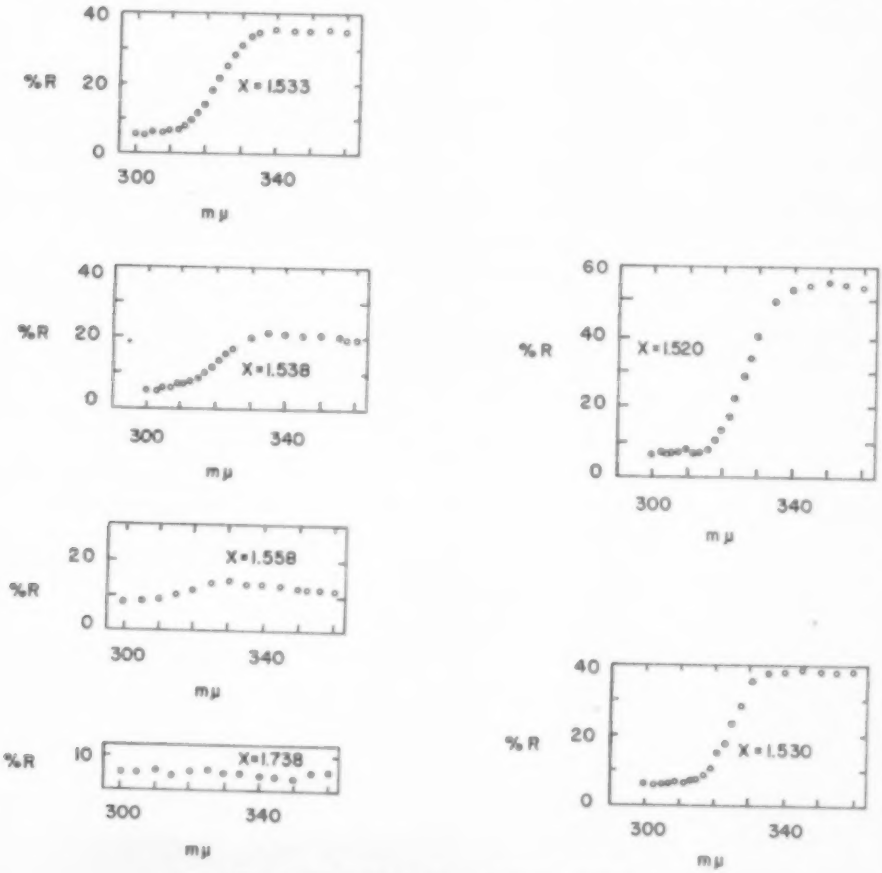

FIG. 1.—Ultra-violet reflectance spectra of PrO_x.

regions, and that as x in PrO_x increases the reflectance decreases. Further, there are relatively distinct absorption bands in the region 400–600 mμ. The ultra-violet cut-off at about 320 mμ corresponds to an energy gap, E_g, which changes in a sigmoidal fashion with composition, see Fig. 4. Beyond the composition $PrO_{1.6}$ significant values of E_g could not be obtained due to the low reflectance for the higher oxides.

[9] R. B. FISCHER and F. VRATNY, *Anal. Chim. Acta* **13**, 588 (1955).
[10] *Spectrophotometry, 200 to 2000 mμ* Circ. No. 484. U.S. Dept. of Commerce, National Bureau of Standards.

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The reflectance of the oxides reach a maximum at about 700 mμ. Figure 5 shows the variation in maximum reflectance vs. composition of the oxide.

A region of low reflectance occurs from about 900 mμ (1·35 eV) into the infra-red. Rather complex electronic transistors associated with the praseodymium ion are

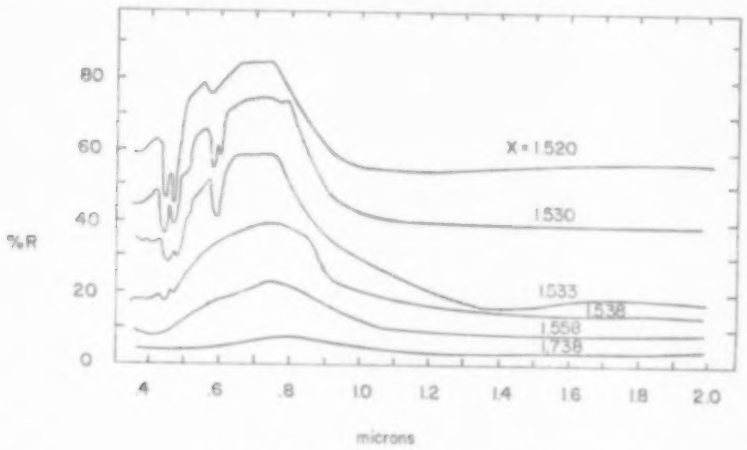

FIG. 2.—Visible-near-infra-red reflectance spectra of PrO_x.

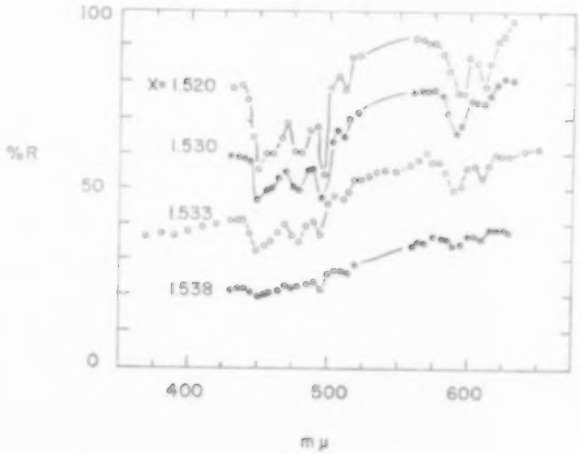

FIG. 3.—Reflectance spectra of PrO_x in the 350–650 mμ region.

noted in the 400–650 mμ region of the spectrum, see Fig. 3. Bands occur at 445, 460, 475 (470–480), 490, 510, 580 and 610 mμ.

Many of these absorption maxima can be correlated with observed bands of the praseodymium ion in aqueous solution. In aqueous $PrCl_3$, the bands at 510 and 610 mμ are not reported[11] and all others appear to be shifted slightly to higher wavelength. In aqueous $Pr(NO_3)_3$, only the bands at 445, 475 and 580 mμ have been observed.[12]

[11] D. M. YOST, H. RUSSELL and C. S. GARNER, *The Rare Earth Elements and their Compounds*. John Wiley, New York (1950).
[12] C. J. RODDEN, *Res. Nat. Bur. Stand.* **26**, 557 (1941).

EPHRAIM and BLOCK[1] who have studied the spectra of the sesquioxides have mentioned the above absorption bands. It would seem apparent that as one passes from the liquid to solid state one might expect a significant change in the field of the central metal ion. This would give the observed changes in the spectra noted above,

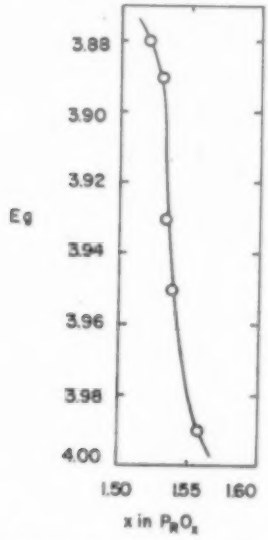

FIG. 4.—Variation in energy gap E_g with composition of PrO_x.

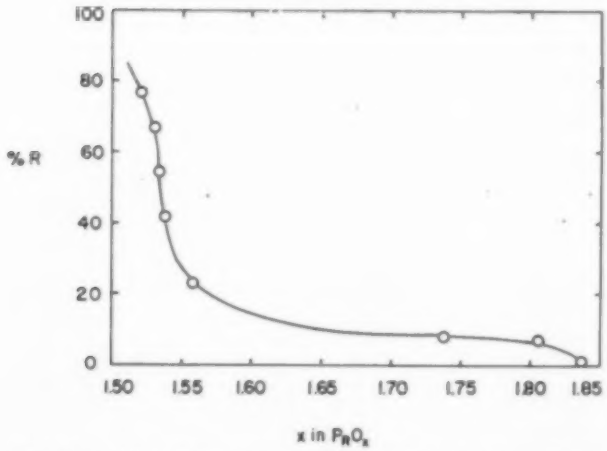

FIG. 5.—Variation in reflectance maximum at 700 mμ with composition of PrO_x.

and would also explain the differences noted in the spectra of the *A* and *C* modification of Pr_2O_3.[1]

Under the conditions of preparation used to obtain the material for this study, the "Pr_2O_3" exists in the hexagonal *A* configuration[13] with a co-ordination number

[13] G. BRAUER and H. GRADINGER, *Z. Anorg. Chem.* 277 89 (1954).

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of seven. This configuration is of a lower symmetry than one would normally expect in solution. As x is increased, further asymmetry must occur, a gradual phase transition to the b.c.c. configuration sets in at $x = 1{\cdot}53$ and is complete at $x = 1{\cdot}65$.[14] It is of interest to note the rapid change in reflectance which occurs at about $x = 1{\cdot}53$, see Fig. 5. The X-ray findings associated with this study have been confirmed on PrO_x in this laboratory.[15]

It is to be noted that the electronic transition of the praseodymium ion cannot be observed beyond a composition of $x = 1{\cdot}56$. At this composition the sample has assumed a brown colour.

For the composition range $1{\cdot}65 \leq x \leq 1{\cdot}80$ the b.c.c. structure predominates, though gradually it gives way to a rhombohedral configuration, with the transition being complete at $x = 1{\cdot}71$. Throughout this region of composition the reflectance of the oxides was nearly constant. A final decrease in reflectance was noted in the region of $PrO_{1{\cdot}83}$.

Work is presently in progress on the electrical properties of these materials. It is felt that a correlation of electrical and optical properties will aid in the understanding of the solid state character of the oxide system PrO_x.

[14] D. J. M. Bevan, *J. Inorg. Nucl. Chem.* **1**, 49 (1955).
[15] Technical Status Report 11, Air Force Office of Scientific Research, S. R. O. M. S. AF 18 (603)-45, December 31, 1958. Unpublished.

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ISOTOPIC TRACER STUDIES ON THE THERMAL DECOMPOSITION OF URANIUM PEROXIDE

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Abstract—Isotopic tracer studies using ^{18}O show that on the decomposition of $UO_4 \cdot 2H_2O$, the oxygen formed originates entirely in the peroxide, and that water is liberated without contamination by "uranyl" or "peroxide" oxygen. The second observation shows that only the oxide formed on decomposition of O_2^{2-} is incorporated into the product UO_3, and also proves that $UO_3 \cdot H_2O_2 \cdot H_2O$ is not a proper constitutional formula of the peroxide.

The conclusions summarized depend on observations for systems in which only partial decomposition has taken place. The products do inter-equilibrate readily, and samples removed after complete decomposition show evidence of this.

ALTHOUGH arguments have been presented for existence of uranium peroxide as a true peroxide hydrate ($UO_4 \cdot 2H_2O$,[1,2] $H_2UO_5 \cdot H_2O$[3]), some authors have considered it to be an addition compound of uranium oxide, $UO_3 \cdot H_2O_2 \cdot H_2O$.[4,5]

Isotope tracer experiments using ^{18}O have been carried out by us in an attempt to differentiate between the two formulations, and to learn something about the course of the decomposition reaction. The products of the decomposition have been variously reported as U_2O_7,[2] UO_3,[6] and $UO_3 \cdot H_2O$[7] (in addition to O_2 and H_2O) and we have therefore also examined and made chemical analyses of the uranium products formed in our experiments.

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EXPERIMENTAL

All of the chemicals used were reagent grade. Baker and Adamson uranyl nitrate hexahydrate was fumed with 70 per cent perchloric acid to remove nitrate ion. The resulting uranyl perchlorate was recrystallized six times using distilled water. Uranium solutions were analysed either by ignition to U_3O_8 or by reduction to uranium(IV) and subsequent titration with cerric sulphate as described elsewhere.[8] Peroxide oxygen was determined by dissolution of the peroxide in cold 1 M H_2SO_4 and subsequent titration with $KMnO_4$. Two samples of uranium peroxide, enriched in ^{18}O, were prepared from solutions of uranyl perchlorate by a modification of the procedure reported by WATT[1]. The solutions were kept cold to minimize isotopic exchange during the precipitation. Both samples were prepared using H_2O_2 of normal isotopic composition and fourfold ^{18}O enriched $UO_2(ClO_4)_2 \cdot 5H_2O$. For sample I, the solvent was enriched 3·43-fold in ^{18}O, and for sample II, 8·69-fold. The resulting precipitates were washed with cold distilled water and dried *in vacuo* to constant weight at room temperature. The powdered samples were stored *in vacuo* over conc. H_2SO_4. (Found: U, 70·0; peroxidic oxygen, 9·40. Calc. for $UO_4 \cdot 2H_2O$: U, 70·4; peroxidic oxygen, 9·46%). The enriched uranyl salt was prepared by heating normal $UO_2(ClO_4)_2 \cdot 5H_2O$ in 0·5 M $HClO_4$ (in eightfold ^{18}O enriched water) solution for 48 hr and purified by recrystallization of the perchlorate.

[1] G. W. WATT, S. L. ACHORN, and J. L. MARLEY, *J. Amer. Chem. Soc.* **72**, 3341 (1950).
[2] J. E. BOGGS and M. EL-CHEHABI, *J. Amer. Chem. Soc.* **79**, 4258 (1957).
[3] R. E. DEMARCO, D. E. RICHARDS, T. J. COLLOPY and R. C. ABBOTT, *J. Amer. Chem. Soc.* **81**, 4167 (1959).
[4] C. DUVAL, *Analyt. Chem. Acta* **3**, 337 (1949).
[5] C. DUVAL, *C.R. Acad. Sci., Paris* **227**, 679 (1948).
[6] R. F. LEININGER, J. P. HUNT, and D. E. KOSHLAND, JR., U.S.A.E.C. TID 5290, Book 2 704–21 (1958). *Chem. Abstr.* **53**, 18712f (1959).
[7] G. TRIDOT, *Ann. Chim.* **10**, 225 (1955).
[8] J. HALPERN and J. G. SMITH, *Canad. J. Chem.* **34**, 1419 (1956).

Samples (0·1–0·2 g) of $UO_4 \cdot 2H_2O$ were placed into a Pyrex vessel on a high vacuum line, evacuated to a pressure of less than 10^{-3} mm Hg and decomposed thermally in a bath of paraffin oil. Water was trapped using a methanol–solid CO_2 slurry. A portion of the oxygen was trapped using liquid nitrogen. Samples of trapped H_2O and UO_3 were heated to 400°C with a mixture of $HgCl_2$ and $Hg(CN)_2$. The carbon dioxide formed was purified for analysis over zinc amalgam at 200°C.[9] The isotope composition of carbon dioxide, thus prepared, and pure oxygen samples were read directly on the mass spectrometer. In all experiments reported, a minimum of 20 per cent decomposition occurred before O_2 or H_2O samples were removed for analysis.

Infra-red absorption spectra were run on KBr disks of the original peroxide, the partially decomposed peroxide, and on the completely decomposed peroxide. The spectra of $UO_4 \cdot 2H_2O$ and the final product, presumably UO_3, agree well with those reported for these compounds in the literature. No evidence was found in the spectra for any hydrated forms of UO_3. The absence of an absorption peak at 1390–1410 cm^{-1} is used as evidence that U_2O_7 was not formed during the *in vacuo* thermal decomposition.[12]

The stoicheiometry of the thermal decomposition was also determined by analysis of the products. In agreement with LEININGER and coworkers,[7] the thermal decomposition of $UO_4 \cdot H_2O$, at temperatures above 150°, can be represented by equation (1).

$$2UO_4 \cdot 2H_2O \rightarrow 2UO_3 + O_2 + 4H_2O \qquad (1)$$

Ignition of the product oxide to U_3O_8 showed it to be 99 per cent pure UO_3. The X-ray diffraction patterns of the product oxide showed it to be amorphous. The oxide also effervesced when dissolved in dilute acid, but it did not decolorize dilute $KMnO_4$ solutions.

RESULTS AND DISCUSSION

The enrichment ratio of Samples I and II is given in Table 1. The entries for H_2O and O_2 correspond to the isotopic composition of the starting material. The enrichment ratio of UO_2^{2+} was calculated from the overall enrichment of the solid peroxide less the enrichment of the water and peroxide.

TABLE 1.—ENRICHMENT RATIOS* OF CONSTITUENTS OF URANYL PEROXIDE

Sample	UO_2^{2+}	H_2O	O_2^{2-}
Sample I	3·61	3·43	1·00
Sample II	5·96	8·69	1·00

* Normal, as measured on this scale, is 1·00.

The results obtained on examining the isotopic composition of the products are presented in Table 2 (O_2) and in Table 3 (H_2O and UO_3). Interchange of oxygen between the products takes place when they are left in contact for extended periods of time at elevated temperatures. Therefore, to learn the isotopic course of the decomposition, the data for experiments in which the gaseous products were removed, and the period of heating was short, should be considered.

Experiments 2.1, 2.2, 2.4, 2.9, and 2.10 show that the oxygen which is given off has substantially the isotopic composition of the peroxide. This confirms the assumption implicit in the entry in Table 1 that the peroxidic oxygen retains its identity. Experiments 3.1, and 3.4 show that H_2O is released without exchange with UO_2^{2+}, and substantially without contamination by peroxidic oxygen. Even in experiment 3.1, ca. 30 per cent of the compound was decomposed, and if the oxide released on decomposition of O_2^{2-} ($2O_2^{2-} \rightarrow 2O^{2-} + O_2$) exchanged with the H_2O, a large decrease in the

[9] M. ANBAR and S. GUTMAN, *J. Appl. Rad. Isotopes* **5**, 233 (1959).

enrichment ratio would have been observed. We infer from the tracer results that the O^{2-} released on the decomposition of the peroxide enters the UO_3 phase. As a corollary of the observations it follows that the constitution is not represented by the formula $UO_3 \cdot H_2O_2 \cdot H_2O$.

Experiments 3.2, 3.3, 3.5, and 3.6 indicate that upon complete decomposition of uranyl peroxide UO_3, H_2O and O_2 do exchange. JOHNSTON *et al.*[10] have shown that oxygen exchange between UO_3 and water was detectable at 25° and the exchange was

TABLE 2.—ENRICHMENT RATIO OF PRODUCT OXYGEN*

Experiment	Conditions	Sample	Enrichment ratio
2.1	20 sec at 170°	I	1·08
2.2	20 min at 170°	I	1·08
2.3	50 min at 170°	I	1·10
2.4	20 sec at 170°	II	1·07
2.5	20 min at 170°	II	1·23
2.6	60 min at 170°	II	1·28
2.7	10 min at 350° O_2 not trapped	II	2·13
2.8	20 min at 200°	II	1·21
2.9	20 sec at 200°	II	1·08
2.10	20 sec at 200°	I	1·04
2.11	30 min at 300° O_2 not trapped	II	2·94
2.12	30 min at 300° O_2 not trapped	I	2·09

* Oxygen gas trapped unless indicated otherwise

TABLE 3. ENRICHMENT RATIO OF PRODUCT UO_3 AND H_2O

Experiment	Conditions	Sample	Enrichment ratio	
			UO_3	H_2O
3.1	10 min at 150°	II	—	8·63
3.2	2 hr at 150°	II	5·42	6·65
3.3	2 hr at 170°	II	5·37	6·16
3.4	5 min at 150°	I	—	3·31
3.5	2 hr at 170°	I	3·09	2·63
3.6	2 hr at 200°	I	3·07	2·72

complete in 4 hr at 100°, presumably by the formation of $UO_3 \cdot H_2O$. From these data it appears that the exchange between UO_3 and H_2O should be complete in several minutes at temperatures above 150° if a hydrated uranium oxide is formed as an intermediate. In our experiments the UO_3 is not at isotopic equilibrium with the water produced after 120 min at 170–200°. Thus, we assume that appreciable amounts of hydrated uranium oxide do not form during the thermal decomposition of uranium peroxide under our conditions. The exchange which takes place on complete decomposition may occur while the gaseous products diffuse through the reaction mixture in which large amounts of UO_3 have accumulated.

[10] F. J. JOHNSTON, D. A. HUTCHINSON and J. J. KATZ, *J. Inorg. Nucl. Chem.* **7**, 392 (1958).

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Experiments 2.7, 2.11, and 2.12 were quite typical of runs in which the oxygen was not trapped during the decomposition. These results might be expected on the basis of studies of the exchange of oxygen between solid oxide and oxygen gas,[10,12] experiments which were characterized by the occurrence of a portion of rapid exchange between the oxide surface and oxygen gas.

On the basis of our experiments we conclude that uranium peroxide is a true peroxide hydrate containing three different oxygens in the ratio of 1 : 1 : 1; that in the temperature range between 160–350° the products of decomposition are UO_3, O_2 and H_2O; that the peroxide oxide becomes part of the UO_3 phase without exchange with product water. The tracer experiments eliminate the formulation of uranium peroxide as $UO_3 \cdot H_2O_2 \cdot H_2O$.

Acknowledgement—This work was supported by the National Science Foundation under Grant No. NSF G–5411.

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[12] J. A. Allen and I. Lauder, *Nature, Lond.* **164,** 142 (1949).

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THE URANIUM(V)-CATALYSED EXCHANGE REACTION BETWEEN URANYL ION AND WATER IN PERCHLORIC ACID SOLUTION

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(*Received* 9 *May* 1960)

Abstract—The exchange reaction between UO_2^{2+} and H_2O was studied at 25°. A method using ferrocyanide ion is described for the direct sampling of uranyl ion. The exchange reaction is catalysed by UO_2^+ which disproportionates with a second order dependence on UO_2^+. The value of the specific rate appropriate to the rate law

$$\frac{-d(UO_2^+)}{dt} = k(H^+)(UO_2^+)^2$$

is found to be 435 at $\mu = 1{\cdot}58$. A mechanism for the exchange reaction is proposed and a minimum value for the rate of electron exchange between U(V) and U(VI) is given. Data for the uncatalysed reaction are also given.

THE exchange between UO_2^{2+} and H_2O has been reported to be very slow,[1] but some test experiments we performed preparatory to carrying out tracer studies on the oxidation of U(IV) showed that the exchange was not dependably slow. Other workers have also observed the rate of exchange to be difficult to reproduce and to vary from one preparation of uranyl salt to another.[2,3,4] We therefore undertook to discover the cause of the induced or catalysed exchange, and to learn just how rapid the intrinsic rate of exchange is.

Previous attempts to study the UO_2^{2+}–H_2O exchange were based on a procedure in which solvent was sampled for isotopic analysis.[1] This method has inherently low sensitivity, and is therefore less accurate than direct sampling of the uranyl ion. We have found that ferrocyanide ion provides a means of sampling the uranyl ion directly and the method based on its use gives analyses of high precision.

EXPERIMENTAL

All of the chemicals used in this work were reagent grade. Uranyl nitrate hexahydrate (Baker and Adamson) was the source of uranyl ion. Baker and Adamson perchloric acid (chloride free) was used to prepare uranyl perchlorate from uranyl nitrate. The uranyl perchlorate was recrystallized from distilled water six times. The resulting crystals were dried *in vacuo* and corresponded to the formula, $UO_2(ClO_4)_2{\cdot}5H_2O$. (Found: U, 42·6. Calc. for $UO_2(ClO_2)_2{\cdot}5H_2O$: U, 42·6%). The pentahydrate was stored in sealed tubes until ready for use.

Uranium analyses were made by electrolytic reduction of UO_2^{2+} in 1 M $HClO_4$ using a Hg cathode and Pt anode in a compartmented cell. Providing the solution was kept cold (0°C) the reduction of U(VI) to U(IV) went to completion. Any U(III) formed was removed by a stream of oxygen. Uranium(IV) was titrated with cerric sulphate at 50° using ferroin as the indicator.

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[1] H. W. CRANDALL, *J. Chem. Phys.* **17**, 602 (1949).
[2] M. ANBAR, Weizmann Institute, private communication (1960).
[3] J. J. KATZ and S. SUJISHI, Argonne National Laboratory, private communication (1960).
[4] I. SHEFT and H. HYMAN, Argonne National Laboratory, private communication (1960).

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The tracer experiments were done by adding perchloric acid solutions, enriched in $H_2{}^{18}O$, to weighed samples of $UO_2(ClO_4)_2 \cdot 5H_2O$. Aliquots of UO_2^{2+} were removed as a function of time, followed by precipitation with an aqueous solution of $K_4Fe(CN)_6$ and subsequent filtration. The detailed procedure used was as follows. The exchange reaction was quenched by the addition of an aliquot containing 0·2 mmole of UO_2^{2+} solution to 0·5 ml of normal H_2O followed by the addition of 0·1 mmole of aqueous $K_4Fe(CN)_6$. The solution was stirred rapidly by means of a magnetic stirrer. Fifty millilitres of acetone was added to aid filtration and the precipitate was collected on a sintered

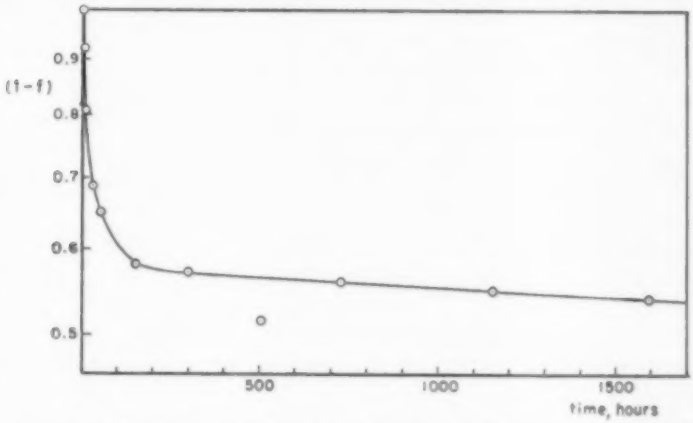

FIG. 1.—McKay plot for exchange of uranyl ion with water. 0·93 M $UO_2(ClO_4)_2$, and 1·00 M $HClO_4$.

glass filter. The precipitate was air dried about 1 min. The medium brown solid was transferred to a 4 ml Pyrex glass ampoule with a break-off tip and a seal-off constriction together with 100 mg of analytical, vacuum dried, anhydrous $HgCl_2$.[5] The ampoule was evacuated to about 10^{-3} mm Hg., degassed, and sealed off under vacuum. The sample tubes were then heated to 400° for 2 hr, cooled and the ampoule was opened on a vacuum line. The gases formed were condensed by liquid N_2 into a second degassed ampoule containing 1–2 g Zn–Hg. The non-condensable gases were pumped off. The second ampoule was sealed off under vacuum and heated for 2 hr at 200°C, converting all the $(CN)_2$ to $Zn(CN)_2$. The ampoule was opened on the vacuum line and the CO_2 was condensed into a closed tube (fitted with a stopcock) using liquid N_2. The isotopic composition of the CO_2 was read directly on the mass spectrometer. The impurities introduced by this method were below the limits of detection with our mass spectrometer.

Europic oxide was used to prepare Eu^{2+} by the method of LINGANE and PECSOK[6] using Zn amalgam. Solutions for use in experiments with Eu_2^+ were degassed several times by repeated freezing and evacuation. The solutions were stored under an atmosphere of Linde High Purity N_2. The reaction vessels were flushed with nitrogen as were the solutions at the beginning of an experiment.

RESULTS AND DISCUSSION

Figure 1 shows a McKAY[7] plot for an exchange experiment with a 0·93 M solution of UO_2^{2+} in 1·0 M $HClO_4$. The kinetic behaviour displayed is typical of the experiments we have done. Although the internal consistency for any one run was excellent, the agreement between similar runs was quite poor, particularly with respect to the rate at which the McKAY plot would become linear. The fact that the McKAY plots are non-linear shows that a net chemical change is taking place in the system, and the only reasonable possibility seems to be that a catalyst is decreasing in concentration

[5] M. ANBAR and S. GUTTMANN, *J. Appl. Rad. Isotopes* **5**, 233 (1959).
[6] J. J. LINGANE and R. L. PECSOK, *Analyt. Chem.* **20**, 425 (1948).
[7] H. A. C. McKAY, *Nature, Lond.* **142**, 997 (1938).

as time increases. Among the possibilities that come to mind for the catalyst are: an impurity not derived from uranium, a lower oxidation state of uranium, some condensed species containing U(VI). The observations[8,9] on the hydrolysis of UO_2^{2+}, however, appear to rule out the last possibility for solutions 1 M in acid, and it is in any case ruled out by the further observations to be cited in the present paper.

Attempts were made to prepare very pure solutions of uranyl perchlorate in perchloric acid by repeated purification using the following scheme. Uranyl perchlorate was crystallized six times from distilled water and then precipitated as the peroxide.[10] The peroxide was heated at 250° *in vacuo* and converted to UO_3.[11] The UO_3 was dissolved in dilute perchloric acid and uranyl perchlorate was recrystallized twice. Uranyl peroxide was reprecipitated and the preceding procedure was repeated three times. Finally, UO_3 was dissolved in 70 per cent perchloric acid and diluted with a known volume of enriched H_2O.* Once again non-linear McKAY plots were obtained.

Table 1 summarizes the results of experiments in which U(VI) solutions were prepared or treated in different ways. Experiments 1.08 and 1.09 show that neither H_2O_2 nor O_2 appreciably catalyse the exchange. Experiment 1.03 in comparison with 1.02 suggests that U(IV) is not the primary catalyst, but the catalyst can be generated from it by UO_2^{2+}. Experiment 1.07 shows that oxidizing agents also are effective. Experiment 1.01 in comparison with 1.04 suggests that a reducing agent, in this case U(III) acting on U(VI) also generates the catalyst. These experiments point to the conclusion that the catalyst is UO_2^{+}. Experiment 1.12 shows that the action of ultra-violet light on UO_2^{2+} solutions also produces the catalyst, and this is again consistent with the view that the catalyst is UO_2^{+}. Light is known to reduce UO_2^{2+},[12,13] and the production of NpO_2^{+} from NpO_2^{2+} is known to take place under the influence of light.[14] HEAL[15] has shown that UO_2^{+} is probably responsible for the shift of the potential of a U(VI)–U(IV) electrode under illumination, and he refers also to the formation of U(V) in mixtures of U(IV) and U(VI).

The study of the decay of the catalyst with time seems to confirm the view that it is indeed U(V). Uranium(V) can be generated substantially quantitatively from U(VI) by using Eu^{2+}.[16] The results of a number of experiments in which Eu^{2+} was added to UO_2^{2+} in solution are presented in Table 2. Included are some experiments with Cr^{2+}, which have special interest in connection with tracer experiments to be discussed in a future publication. Experiments 2.01 and 2.02 show that UO_2^{+} (as generated by Eu^{2+}) does indeed catalyse the exchange. Experiment 2.03 is a blank experiment using Eu^{3+} and substantially no catalysis occurs. Experiment 2.08 (along with its blank experiment, 2.09) shows that Cr^{2+} will also catalyse the exchange.

The data for an experiment designed especially to follow the rate of decay of the catalyst are presented in Table 3.

* Starting time of the reaction was taken to be the time of addition of the enriched H_2O.

[8] S. AHRLAND, *Acta Chim. Scand.* **3**, 374 (1949).
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[16] T. NEWTON and H. TAUBE. To be published.

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TABLE 1.—CATALYSIS OF THE EXCHANGE BETWEEN URANYL ION AND WATER AT 25°C

Experiment	Source of uranyl ion	mmole of 1·00 M UO_2^{2+} used	Substance added to catalyse exchange	Time	Fraction of exchange
1.00	$UO_2(ClO_4)_2 \cdot 5H_2O$	2	—	60 sec	0·000
1.01	$UO_2(ClO_4)_2 \cdot 5H_2O$	2	0·1 mmole fresh U(IV)*	40 sec	0·045
1.02	$UO_2(ClO_4)_2 \cdot 5H_2O$	2	0·1 mmole fresh U(IV),* no UO_2^{2+}, aged 100 min	40 sec	0·015
1.03	$UO_2(ClO_4)_2 \cdot 5H_2O$	2	0·1 mmole U(IV),* 0·1 mmole U(VI) aged 10 min	40 sec	0·133
1.04	$UO_2(ClO_4)_2 \cdot 5H_2O$	2	0·1 mmole U(IV),‡ U(III) not removed after electrolytic reduction	40 sec	0·256
1.05	$UO_2(ClO_4)_2 \cdot 5H_2O$	2	0·1 mmole fresh U(IV) (0·5 M $HClO_4$)	40 sec	0·030
1.07	$UO_2(ClO_4)_2 \cdot 5H_2O$	2	0·2 mmole U(IV)* + 0·1 mmole H_2O_2	40 sec	0·295
1.08	$UO_2(ClO_4)_2 \cdot 5H_2O$	2	0·2 mmole H_2O_2	10 sec	0·000
1.09	$UO_2(ClO_4)_2 \cdot 5H_2O$	2	O_2 gas bubbled through solution for 120 sec	120 sec	0·000
1.10	UO_3 in $HClO_4$	1	—	60 sec	0·546
1.11	UO_3 in $HClO_4$	1	—	60 sec	0·480
1.12	$UO_2(ClO_4)_2 \cdot 5H_2O$	1	Solution† of UO_2^{2+} exposed to Hg arc, 2537Å, for 20 min‡	20 hr	0·115

* U(IV) solutions prepared electrolytically, solutions 1·0 M in $HClO_4$ and U(III) present removed by bubbling O_2 through the solution.
† Aged solution of UO_2^{2+} used in which $t_{1/2}$ for exchange was $\sim 10^6$ hr.
‡ 1·00 M in $HClO_4$.

TABLE 2.—CATALYSIS OF EXCHANGE BETWEEN URANYL ION AND WATER BY URANIUM(V) (AS GENERATED BY Eu^{2+} AND Cr^{2+})

Experiment	Temperature (°C)	Concentration of solution added (mole/l.)	Time	Fraction exchange
2.01	25	0·004 Eu^{2+}**	40 sec	0·286
2.02	0	0·0013 Eu^{2+}, 0·6 M H^+†	40 sec	0·158
2.03	25	0·004 Eu^{2+}*	40 sec	0·026
2.04	25	$9{\cdot}0_2 \times 10^{-4}$ M Eu^{2+}**	0·62 min ‡	0·423
2.05	25	$9{\cdot}0_2 \times 10^{-4}$ M Eu^{2+}**	1·17 min‡	0·451
2.06	25	$9{\cdot}0_2 \times 10^{-4}$ M Eu^{2+}**	2·17 min‡	0·484
2.07	25	$9{\cdot}0_2 \times 10^{-4}$ M Eu^{2+}**	4·00 min‡	0·527
2.08	25	0·01 Cr^{2+}**	40 sec	0·186
2.09	25	0·01 Cr^{2+}**	40 sec	0·027

* Added to 1·0 mmole of 1·00 M UO_2^{2+} in 1·00 M $HClO_4$.
† Eu^{2+} was added to UO_2^{2+}, stored for 10 sec then added to 1·00 mmole of UO_2^{2+}, in 1 M $HClO_4$.
‡ t from time $9{\cdot}0_2 \times 10^{-4}$ M Eu^{2+} was added to UO_2^{2+}
** Added to 5·00 mmoles of 0·50 M UO_2^{2+} in 1·00 M $HClO_4$.

If we accept the assumption that the rate of the catalysed exchange between UO_2^{2+} and H_2O is first order in UO_2^+, then the half-life for the UO_2^{2+}–H_2O exchange at any instant ($t^i_{1/2}$) is inversely proportional to the concentration of the catalyst. Now if UO_2^+ disappears by a second order reaction, as in the experiments on its disproportionation done by KERN and ORLEMANN[17], then

$$t^i_{1/2} \text{ which is } \left[\frac{1}{(UO_2^+)}\right]$$

should increase linearly with t, the time of reaction. Fig. 2 presents the results which are obtained when the data of Table 3 are treated as implied. The values of $t_{\frac{1}{2}}^i$ were obtained by taking slopes in the MCKAY plot of the data of Table 3. The results

TABLE 3.—DECAY OF URANIUM(V) CATALYST AS A FUNCTION OF TIME FOR 0·50 M $UO_2(ClO_4)_2$ SOLUTION IN 0·0811 M $HClO_4$*

t (min)	$^{18}O/^{16}O$ (as CO_2)	$(1-f)$
—	0·004075	—
0·367	0·004336	0·980
1·00	0·004700	0·951
2·00	0·005134	0·917
4·00	0·005678	0·873
8·00	0·006200	0·832
15·0	0·006305	0·824
30·0	0·006375	0·818
60·0	0·006394	0·817
150	0·006461	0·812
300	0·006473	0·811
600	0·006562	0·804
1500	0·006858	0·780
∞	0·016700†	—

* UO_2^+ initially generated at $7{\cdot}2 \times 10^{-4}$ M.
† Calculated on basis of mole fraction of solute and solvent.

of Fig. 2 confirm the second-order law for the disappearance of the catalyst. The initial concentration is taken to be equivalent to the Eu^{2+} added and from the slope and intercept the specific rate for the disproportionation can be calculated. The value of specific rate appropriate to the rate law[17]

$$-d(UO_2^+)/dt = k(H^+)(UO_2^+)^2$$

is found to be 435 M^{-2} sec^{-1}. KERN and ORLEMANN report values of k in the range of $\mu = 0{\cdot}1$–$0{\cdot}4$, k increasing with μ and reaching a value of 135 at $\mu = 0{\cdot}4$. Our value obtained at $\mu = 1{\cdot}58$ is therefore consistent with theirs.

The deviation from linearity in Fig. 2 after four half-lives indicates that U(V) is also being removed by some process less than second order in UO_2^+, and this may be by air oxidation.

The data in Fig. 1 have been treated in a similar manner. A graph of ($t^i_{1/2}$) against (t) is linear and, assuming an extrapolated value of 600 for k in a solution

[17] D. M. H. KERN and E. F. ORLEMANN, *J. Amer. Chem. Soc.* **71**, 2102 (1949).

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of $\mu = 3{\cdot}8$, we calculate an initial concentration of U(V) present in the 0·93 M UO_2^{2+} solution as $1{\cdot}2 \times 10^{-6}$ M.

Experiments 2.03–2.07 consist of the data collected for an experiment using 0·50 M UO_2^{2+} in 1·00 M $HClO_4$. The specific rate constant for the disproportionation of UO_2^+ at the higher ionic strength prevailing is expected to be ca. 6×10^2. The first sample was taken at the end of 37 sec, and only 1/32 of the original U(V) should be left (~five half-lives have passed). Treatment of these data in the manner described results in a value of $k \approx 4 \times 10^2$, which is in reasonable agreement with our other values.

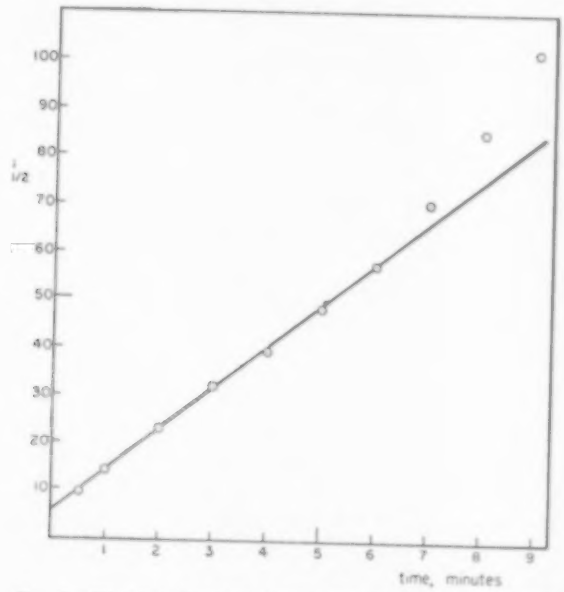

FIG. 2.—Kinetics of catalyst decay (see text) for 0·5 M $UO_2(ClO_4)_2$ in 0·0811 M $HClO_4$ with UO_2^+ generated at $7{\cdot}2 \times 10^{-4}$ M (initial).

We suggest that the mechanism for the catalysed exchange is as follows:

$$UO_2^+ + H_2O^* \rightarrow UO_2^{*+} + H_2O$$

$$UO_2^{*+} + UO_2^{2+} \rightarrow UO_2^{*2+} + UO_2^+$$

If this mechanism is accepted, we can calculate a minimum value of the rate of electron exchange between U(V) and U(VI), knowing the value of UO_2^+ appropriate to a particular value of $t_{1/2}^i$, and the value of the UO_2^{2+} concentration. A value of 52·0 M^{-1} sec^{-1} is calculated for 1·0 M $HClO_4$ and 2·9 M^{-1} sec^{-1} for 0·0811 M $HClO_4$. Our value of 52·0 M^{-1} sec^{-1} is consistent with a value of 110 M^{-1} sec^{-1} extrapolated from the NpO_2^{2+}–NpO_2^+ systems as reported by COHEN *et al.*[18]

In view of the weak dependence of the rate of electron exchange for the NpO_2^{2+}–NpO_2^+ system on hydrogen ion concentration, it is unlikely that the value of the lower limit for the specific rate at low acid actually measures the rate of electron transfer, and it is more likely that at low acid the rate of oxygen exchange between

[18] D. COHEN, J. C. SULLIVAN and J. C. HINDMAN, *J Amer. Chem. Soc.* **76**, 352 (1954).

UO_2^+ and H_2O becomes rate determining. This in turn suggests that the substitution lability of UO_2^+ increases with acidity. Another result of great interest is derived from the comparison of the substitution lability of UO_2^+ with that of UO_2^{2+} (the latter as determined in experiments to be outlined following this paragraph). If the mechanism as represented above describes the catalysed UO_2^{2+}–H_2O exchange, then the rate of oxygen exchange between UO_2^+ and H_2O must be equal to, or exceed, the rate of oxygen exchange between UO_2^{2+} and H_2O as catalysed by UO_2^+. Now from Fig. 2, taking $t_{1/2}^f = 5$ min when $(UO_2^+) = 7{\cdot}2 \times 10^{-4}$,

$$k_1(UO_2^+) \geq k_2(UO_2^{2+})$$

or

$$k_1 \geq \frac{(0{\cdot}69)(0{\cdot}50)}{(5)(60)(7{\cdot}2 \times 10^{-4})} = 1{\cdot}6 \text{ sec}^{-1}$$

where k_1 is the specific rate for the UO_2^+–H_2O exchange. The specific rate for the intrinsic UO_2^{2+}–H_2O exchange by a first order process is $<1{\cdot}6 \times 10^{-7}$, so that the

TABLE 4.—EXCHANGE EXPERIMENTS BETWEEN UO_2^{2+} AND H_2O IN PERCHLORIC ACID SOLUTIONS

(UO_2^{2+}) mole/l.	(H^+) mole/l.	Misc.	$t_{1/2}$ (hr)
0·5	1·0	Cl_2	$7{\cdot}5 \times 10^3$
1·0	1·0	Cl_2	$4{\cdot}0 \times 10^3$
0·5	0·081	Cl_2	575

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labilities of UO_2^+ and UO_2^{2+} differ by a factor of at least 10^7 in 0·0811 M $HClO_4$.

The specific rate for the intrinsic UO_2^{2+} exchange in 1·00 M $HClO_4$ is $<4{\cdot}8 \times 10^{-8}$ and the lower limit for the specific rate for the UO_2^+–H_2O exchange in 1·00 M $HClO_4$ is $1{\cdot}8 \times 10^2$. Thus the labilities of UO_2^+ and UO_2^{2+} in 1·00 M $HClO_4$ differ by at least 3×10^9.

Three other experiments are summarized in Table 4. These experiments were done in solutions through which Cl_2 gas had been bubbled prior to the mixing of UO_2^{2+} and H_2O.† The MCKAY plots are linear and the $t_{\frac{1}{2}}$ values are listed in the table. The data indicate quite clearly that exchange reaction between UO_2^{2+} and H_2O has a negative hydrogen ion dependence These experiments were not done at constant ionic strength and certainly suggest that the UO_2^{2+}–H_2O system be investigated in more detail. The fact that Cl_2 rapidly destroys the active catalyst is itself the strongest proof that the catalyst is not U(IV)—U(IV) reacts only slowly with Cl_2.

Acknowledgement—This work was supported by the National Science Foundation under Contract No. NSF G-5411.

† It appears the Cl_2 quantitatively oxidizes UO_2^+.

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THE THERMAL DECOMPOSITION OF LANTHANUM OXALATE*

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Abstract—Anhydrous lanthanum oxalate is stable at 320°C. On heating this salt at higher temperatures intermediates are produced which appear to correspond to definite compositions, but they are contaminated with finely dispersed carbon. The course of the decomposition in vacuum, as followed by measuring the increase of pressure, is typical of some branching chain reactions in solids, and Prout and Tompkins' equation applies.

The constant high proportion of carbon dioxide in the evolving gases, the infra-red spectra of the solid residues and other experimental results, are explained by the initial conversion of the oxalate into carbonate and carbon monoxide. The latter disproportionates into carbon dioxide and carbon, under the high pressure existing in the channels through which the gases surge out of the decomposing crystallites.

The compositions of the intermediates obtained at temperatures up to 420°C are given in Table 4. The activation energy of the initial decomposition of the oxalate is 31·7 kcal/mole.

THIS work was begun with the intention of making a comparative study of the thermal behaviour and the kinetics of decomposition of the rare earth oxalates. It was also of interest to know whether stable anhydrous oxalates[1] and intermediate carbonates may be prepared by this method. In the course of this study some further problems arose. Of these the following should be mentioned:

(a) The route by which an oxalate decomposes. In some cases (e.g. the oxalates of the alkaline earths),[2] decomposition is represented by the equation: $C_2O_4^{2-} \rightarrow CO_3^{2-} + CO$, followed at higher temperatures by: $CO_3^{2-} \rightarrow O^{2-} + CO_2$ yielding equal volumes of carbon monoxide and carbon dioxide when the oxalate has been completely decomposed to the oxide. With other oxalates (e.g. silver and nickel)[3] the metal is produced:

$$MC_2O_4 \rightarrow M + 2CO_2.$$

Lastly, the decomposition of lead oxalate[4] seems to follow both routes simultaneously.

(b) How far the disproportionation[5] of carbon monoxide:

$$2CO \rightleftharpoons C + CO_2$$

* A part of this article was read before the XVIIth International Congress of Pure and Applied Chemistry (A337) Munich, Sept. 1959.

** This article is taken partly from a Ph.D. thesis submitted by M. STEINBERG to the Senate of the Hebrew University, Jerusalem, 1959.

[1] A. GLASNER and M. STEINBERG, *Bull. Res. Council Israel* **8** A, 174 (1959).

[2] H. N. TEREM and S. TÜCCARBASI, *Istanbul Üniversitesi Fen Fakültesi Mecmuasi* C **23**, 14 (1958); H. PETERS and H. G. WIEDEMANN, *Z. Anorg. Chem.* **300**, 142 (1959).

[3] A. FINCH, P. W. M. JACOBS and F. C. TOMPKINS, *J. Chem. Soc.* 2053 (1954). Z. G. SZABÓ and E. BIRÓ-SUGÁR, *Z. Elektrochem.* **60**, 869 (1956); J. A. ALLEN and D. E. SCAIFE, *J. Phys. Chem.* **58**, 667 (1954); V. DANEŠ and V. PONEC, *Coll. Czech. Chem. Comm.* **23**, 848 (1958).

[4a] L. L. BIRCUMSHAW and I. HARRIS, *J. Chem. Soc.* 1898 (1948); [b] P. E. YANKWICH and J. L. COPELAND, *J. Amer. Chem. Soc.* **79**, 2081 (1957).

[5] S. OTT, *Z. Physik. Chem.* **109**, 1 (1924); R. W. M. D'EYE and P. G. SELLMANN, *J. Inorg. Nucl. Chem.* **1**, 143 (1955).

(commonly referred to as the Boudouard reaction), affects the ratio of the two carbon oxides in the evolving gases.

The information available in the literature on the thermal decomposition of the rare earth oxalates is rather scanty, mostly of a preliminary nature.[6] This article reports our results with lanthanum oxalate only.

EXPERIMENTAL

The lanthanum oxalate used and its mode of preparation, have already been described in previous publications.[7]

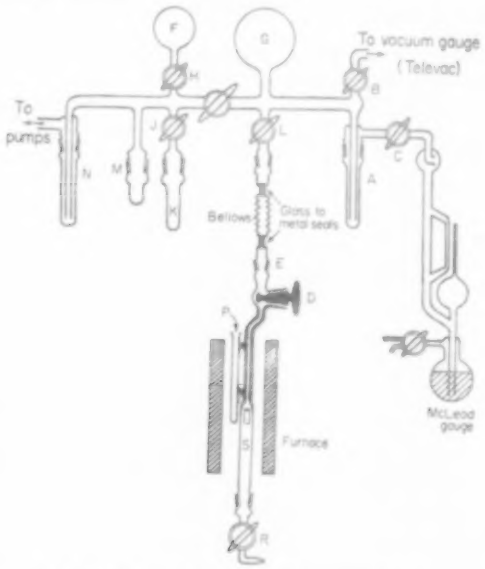

FIG. 1.—Vacuum apparatus and reaction vessel.

The vacuum apparatus. Figure 1 represents diagrammatically the reaction vessel and the vacuum apparatus. The apparatus was evacuated 12 hr before each run in order to ensure that there was no leakage. The bulb *F* of known volume (529 ml) served to estimate the volume of the rest of the apparatus, which was 4220 ml. In comparison, the volume of the part of the reaction vessel surrounded by the electric oven was less than 10 ml. During a run, pressures were measured continuously by a Televac (Frederick & Co.), having a scale in the range 0–1000 μ, calibrated for air by the manufacturer. Measurements were also made at fixed intervals with the McLeod gauge. The readings on the two pressure gauges agreed in the absence of water vapour up to about 300 μ. The traps *A* and *N* were cooled by a Dry-Ice–acetone mixture.

The reaction vessel. *S* was made of Pyrex glass and had a total volume of about 20 ml. A chrome–nickel wire was fastened to the winch D and supported a silver crucible with the weighed sample (5–17 mg, weighed to $\pm$0·01 mg.) The silver crucible was raised to the position shown in the diagram, just when an experiment was begun, after the adjustment of the temperature. The open tube *P* carried the measuring bulb of a "Fielden thermostat"; its lower end was just opposite the silver crucible and positioned symmetrically with reference to the cylindrical oven. A hook soldered to the bottom of the crucible helped to remove it when a run was over, and the residue was reweighed.

[6] C. DUVAL, *Inorganic Thermogravimetric Analysis* pp. 400–416. Elsevier, Amsterdam (1953); W. W. WENDLANDT *Analyt. Chem.* **30**, 58 (1958); **31**, 408 (1959); P. L. GÜNTHER and H. REHAAG, *Ber. Dtsch. Chem. Ges.* **71** B, 1771 (1938); H. J. BACKER and K. H. KLAASSENS, *Z. Anal. Chem.* **81**, 104 (1930).

[7] A. GLASNER, M. STEINBERG and E. LEVY, *Chemist-Analyst* **48**, 37 (1959); A. GLASNER and M. STEINBERG, *Analyt. Chem.* **31**, 1922 (1959).

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In a blank with two thermocouples, the one placed in P and the other one inside the reaction vessel touching the silver crucible, it was observed that the readings equalized within half a minute, but the solid sample might have reached the fixed temperature only after a minute or two. It is thought that in all experiments the temperatures were kept constant to $\pm 0{\cdot}2$°C.

Composition of gaseous products. On exchanging the cooling mixture around the traps A and N for liquid air, carbon dioxide, but not carbon monoxide[48,8] present in the evolving gases, was condensed. Thus the final partial pressures of these two gases were ascertained.

Preparation of samples. Batches of lanthanum oxalate (sufficient for a large number of experiments) were carefully dehydrated at 300°C in vacuum.[1] Tube K served for this purpose. The

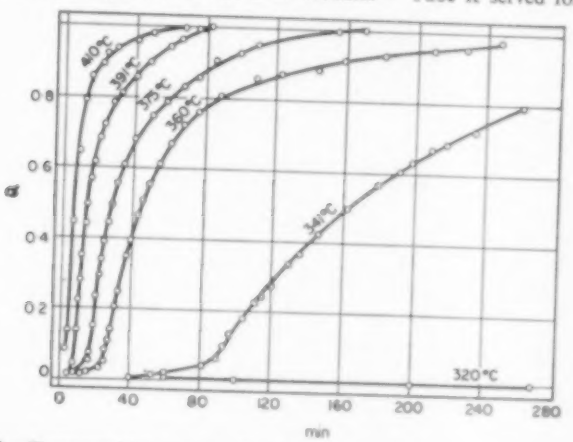

FIG. 2.—Decomposition curves of lanthanum oxalate in vacuum, at constant temperatures, showing fraction of final pressure α at time t in minutes.

dehydration was kept under control by ascertaining that the loss of weight equalled that of the water of crystallization, and that there was no rise of pressure in the apparatus when the water vapours condensed in the cold traps, a proof that the oxalate did not decompose.

The thermobalance. A few experiments were made with a Stanton thermobalance in air. The rate of heating was 6·6°C per min, and the temperature was recorded to an accuracy of ± 2°C.

Infra-red spectra of the solid residues, after decomposition at fixed temperatures in vacuum, were taken by the potassium bromide disk method, with a Baird recording infra-red spectrophotometer. These spectra revealed the presence or absence of the oxalate and/or the carbonate ions in the residue, and served as a qualitative confirmation for conclusions arrived at by the other methods.

RESULTS

Thermal decompositions in vacuum of the dehydrated lanthanum oxalate were made in the temperature range 320°—420°C, at about 20°C intervals. The increase of pressure with time was recorded until a constant final pressure (P_f) was reached which did not change any more for at least 1 hr. The results thus obtained were plotted in Fig. 2 as the fraction of the final pressure (α) versus time. No rise in pressure was observed at 320°, i.e. no decomposition took place at that temperature (after 9 hr heating). The absence of a temporary rise of pressure should also be noted, this being an indication that the oxalate samples were completely dehydrated (otherwise a sharp kick, lasting a few minutes, is recorded on the "Televac" owing to a lag in the condensation of the water vapours).

At higher temperatures the decomposition curves are sigmoidal, characteristic for decompositions of solids of this type, and fairly well reproducible. The induction

[8] J. H. EDGERTON and H. G. DAVIS, U.S.A.E.C. ORNL-2211 (1957).

period (being the least reproducible) lasted over one hour at 341°, and rapidly decreased on increasing the temperature.

The partial pressures of carbon dioxide and carbon monoxide at the end of a run are recorded in Table 1. The sum of these partial pressures is equal to the final pressure (P_f) actually measured. In the Table are also given the weights of the samples, and the final pressures expected, supposing the conversion of oxalate to carbonate:

$$C_2O_4^{2-} \rightarrow CO_3^{2-} + CO$$

(10 mg of anhydrous $La_2(C_2O_4)_3$ should give in the apparatus employed a pressure of 240 μ, at room temperature, 20°C).

TABLE 1.—FINAL PRESSURES AND THE COMPOSITION OF GASES EVOLVED

°C	Sample weight (mg)	Press. exptd. (μ)	Partial pressure		Loss of weight	
			CO (μ)	CO_2 (μ)	Calc. (mg)	Weighed (mg)
341	5·30	127·2	20·2	24·1	0·38	
360	11·35	272·4	74	82	1·31	1·26
375	7·93	190·3	57	68·5	1·07	1·10
391	16·66	400·0	105·3	142·3	2·13	2·12
410	7·08	170 0	54	91	1·27	1·20
420	7·40	177·6	59	115	1·55	1·60

The total pressure obtained at any temperature was proportionate to the weight of the samples, and the ratio of carbon dioxide to carbon monoxide was found to be the same even if some of the experimental conditions were varied (see below).

The comparison of the calculated weight of the gases evolved with the loss of weight obtained by reweighing the residue is very satisfactory, considering the technical difficulties involved in these operations.

All residues were homogeneously coloured brown.

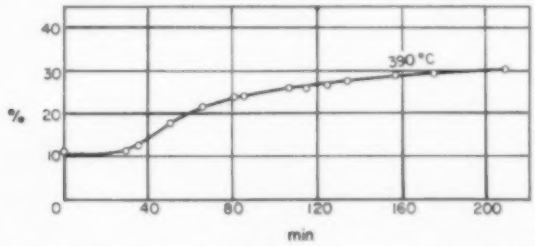

FIG. 3.—Loss of weight of lanthanum oxalate when heated in air at 390°C.

The higher partial pressures of carbon dioxide over those of carbon monoxide, at all temperatures, are striking. This may have resulted either from a reduction of the lanthanum, or a disproportionation of the carbon monoxide. The dark colour of the residue indicated that disproportionation had occurred. Further proof for this conjecture is given in the following.

Thermal decomposition in air. Fig. 3 shows the loss of weight versus time of a

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sample of lanthanum oxalate hydrate when heated on the Stanton balance at a constant temperature, 390°C. (The part of the curve corresponding to the heating up from room temperature is not recorded). No further loss in weight occurred after about 210 min, and the weight of the white residue equalled that calculated for lanthanum carbonate $La_2(CO_3)_3$.

Infra-red spectra. Two of the full spectra taken with solid residues obtained from the vacuum experiments are shown in Fig. 4. The one with the sample heated at 320°C is very much the same as that recorded in the literature[9] for calcium and other oxalates. The spectrum of the residue obtained at 420° is that of a carbonate. The

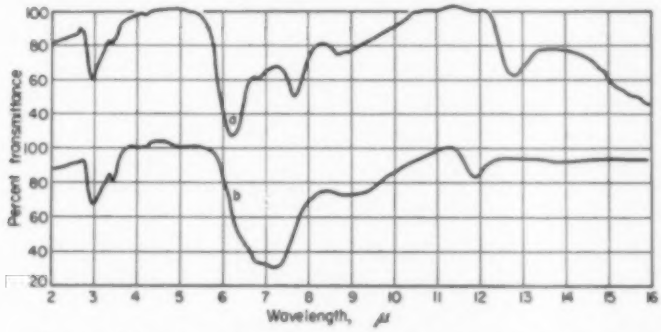

FIG. 4.—Infra-red spectra of samples of lanthanum oxalate after having been heated (a) at 320°, (b) at 420°C.

spectra of the residues at lower temperatures (375°, 391°C) show prominent absorption peaks characteristic for a carbonate, whilst those of the oxalate are very weak. All spectra show the band peaking at 2·95 μ due to water absorbed by the potassium bromide powder.

The ratio of carbon dioxide to carbon monoxide (R), and reproducibility of results. In order to find out whether R is inherent in the thermal reaction or whether it is dependent on external factors, two runs were made in vacuum at 391° under changed experimental conditions:

(a) In one of these runs the carbon dioxide was condensed in traps A and N by liquid air, while the pumps worked continuously. When the reaction was over, the taps isolating the vacuum apparatus from the pumps were closed, and the liquid air traps were exchanged for the usual carbon dioxide–acetone mixture, thereby releasing the condensed carbon dioxide produced in the reaction. The pressure of the carbon dioxide thus released was proportionately equal to the weight of the samples in the regular runs.

(b) The carbon dioxide was condensed as in (a), and only the pressure of the evolving carbon monoxide was measured continuously. Figure 5 shows the pressure time curve thus obtained. The final pressure of carbon monoxide as well as the amount of condensed carbon dioxide were again proportionately equal to the weight of the samples in the regular runs. But on plotting α (the fraction of the final pressure) against time, as in Fig. 2, the resulting curve covered the 391°C curve in Fig. 2 only up to about $\alpha = 0{\cdot}4$. The seemingly faster reaction of the second half of the decomposition is probably due to a lag in the condensation of the carbon dioxide.

Kinetics. On applying Prout and Tompkins' equation,[10] $\ln [\alpha/(1 - \alpha)] = kt + c$, to the sigmoidal decomposition curves, it was found that the experimental points lie

[9] J. M. HUNT, M. P. WISHERD and L. C. BONHAM, *Analyt. Chem.* **22**, 1478 (1950); F. A. MILLER and C. A. WILKINS, *Ibid.* **24**, 1253 (1952).
[10] W. E. GARNER (Editor) *Chemistry of the Solid State* pp. 196–7. Butterworths Scientific Publications, London (1955).

on two straight lines. The points of intersection progress from 33 to 49·5 per cent decomposition as the temperature increases. The reaction constants k_a (acceleratory) and K_d (decay), corresponding to the slopes of these straight lines, are recorded in Table 2. The Table also shows the induction periods t_0 obtained by extrapolating the maximum rate back to zero pressure. The activation energies (E) were calculated by plotting the logarithms of these values against the inverse of absolute temperatures, Fig. 6.

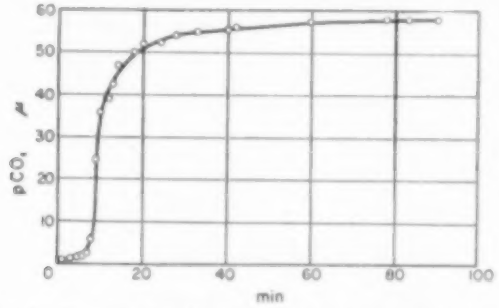

FIG. 5.—Pressure of carbon monoxide vs. time (minutes) on heating lanthanum oxalate at 391°C.

The energy values obtained from the constants k are equivocal. The apparent activation energy calculated from t_0 appears to be 25 per cent higher, i.e. the induction period is regulated by a different mechanism to that of the main reaction.

The decomposition curves given in Fig. 2 were replotted in Fig. 7, using a different time scale for each temperature, i.e. Fig. 7 displays a plot of α versus ft, where f is an appropriate function of the activation energy 31·7 kcal/mole. (The authors are most thankful to the referee for directing their attention to this mode of presentation).

TABLE 2.—RATE CONSTANTS AT VARIOUS TEMPERATURES, AND ACTIVATION ENERGIES (E) CALCULATED THEREFROM

°C	$k_a \times 10^3$	$k_d \times 10^3$	t_0(min.)
341	6·77	1·46	80
360	16·47	3·40	24
375	27·64	5·27	15
391	54·12	9·62	7
410	93·96	19·64	3
E(kcal)	31·7	30·9	39·1

The drawn out line is a copy of the original curve at 360°C. The experimental points obtained at the various temperatures are seen to lie closely on both sides of this curve, excepting the run at 341°C. It should however be noted that the points are regularly displaced to the right, all the more the lower the temperature. Considering that the temperature coefficient of the induction period is larger than that of the main reaction, this result was expected.

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DISCUSSION

The infra-red spectra of residues obtained in the temperature range 360–390°C indicate that the oxalate has been virtually completely decomposed at these temperatures and converted into a carbonate. This is confirmed by the loss of weight obtained with the experiment on the thermobalance at 390° in air.

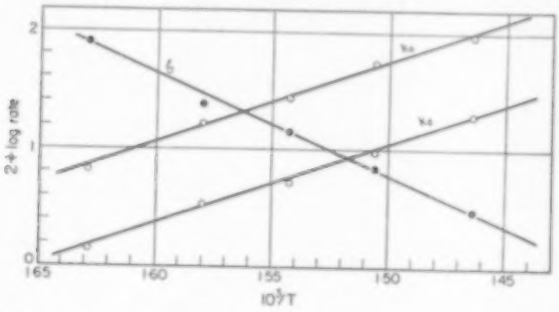

FIG. 6.—Logarithms of rate against inverse of absolute temperature.

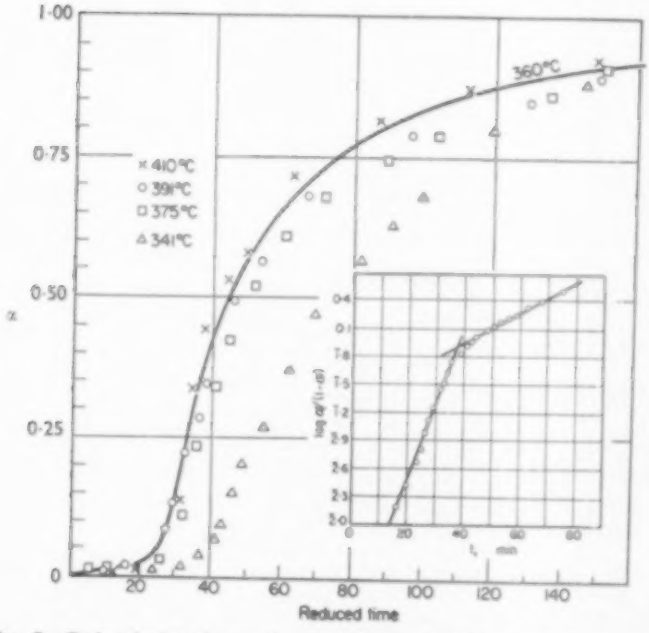

FIG. 7.—Reduced plot of α vs. *ft*. Insert shows plot of log [α/(1 − α)] vs. time in minutes, at 360°C.

A quantitative analysis of the residues with larger samples is impeded by the formation of very finely divided carbon. The amount of carbon dioxide evolved when these samples are treated with acid is only about 70 per cent of the theoretical, and the brown solution slowly decolorized permanganate, quite unlike the reaction with oxalic acid. (The latter experiments were carried out by Mr. E. LEVY, who is continuing the investigation of this problem). Evidently the finely dispersed carbon reduces permanganate as well as a part of the carbon dioxide evolved on treating the residue with acid.

The carbon monoxide collected in the vacuum experiments at all temperatures is only about 30 per cent of the gas that should have been evolved according to all experimental indications (see Table 1). The amount of carbon dioxide, on the other hand, surpasses that which could have been produced by further decomposition of the carbonate to the oxide. That the carbon dioxide originates from a reaction involving reduction of the lanthanum to the divalent state: $La_2(C_2O_4)_3 \rightarrow 2LaC_2O_4 + 2CO_2$ is improbable, and contradicts most of the experimental evidence. For example, in the run quoted in Table 1 at 391°C. a combination of this reaction together with the conversion of 70 per cent of the oxalate into carbonate would imply the evolution of

TABLE 3.—COMPOSITION OF SOLID RESIDUES OBTAINED IN VACUUM, AND THE RATIO $\mu CO_2/\mu CO (= R)$ DUE TO DISPROPORTIONATION

°C	Oxalate decompn. (%)	Best formula of residue	R
341	53·8	$La_2(C_2O_4)_{1\cdot5}(CO_3)_{1\cdot5}$	1·20
360	87·4	$La_2(CO_3)_3$	1·11
375	101·9	$La_2(CO_3)_3$	1·20
391	97·7	$La_2(CO_3)_3$	1·35
410	100·0	$La_2O_{0\cdot6}(CO_3)_{2\cdot4}$	1·08
420	100·0	$La_2O\cdot(CO_3)_2$	1·00

280 and 240 μ of carbon monoxide and carbon dioxide respectively, in complete discord with the partial pressures actually obtained. Hence, as already indicated, the only possible explanation of the phenomena is the disproportionation of the carbon monoxide primarily formed from the oxalate. This line of approach is also indicated by the surprisingly small total pressures obtained with all runs below 410° (in spite of the disappearance of the oxalate bands from the infra-red spectra of the residues), as disproportionation of carbon monoxide involves the reduction of pressure to 50 per cent of what would have been caused by carbon monoxide alone.

Having shown that the carbon dioxide originated from disproportionation of carbon monoxide, and considering that the volume of the gas is halved by this reaction, the percentage q of oxalate converted into the carbonate may be estimated from the partial pressures of the two gases recorded in Table 1:

$$q = 100(\mu CO + 2\mu CO_2)/a,$$

when a is pressure expected, in microns.

It may be seen that in the temperature range 360–391°C the conversion is quantitative in the limits of probable errors. At 341°C only slightly more than 50 per cent of the oxalate has decomposed, and at 410° and 420°C the increased partial pressure of carbon dioxide indicates the commencement of the decomposition of the carbonate. These results are summarized in Table 3 (disregarding the elementary carbon present).

BACKER and KLAASSENS[6] state that on heating lanthanum oxalate at 400° a compound having the composition La_2CO_5 is obtained. This corresponds to the oxycarbonate $La_2O_2\cdot CO_3$, which contains only half the amount of carbonate present in the residue that has been obtained in this work at 420°C.

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It is of interest to note the constancy of R, averaging 1·2 (a disproportionation of over 70 per cent of the carbon monoxide evolved) for runs in which the carbonate does not decompose. This same value is also obtained at 341° when only half of the oxalate is converted to the carbonate, showing that the ratio of carbon dioxide to carbon monoxide evolved is the same at all stages of decomposition. Also, the runs made with liquid air traps, condensing the carbon dioxide, and with continued pumping, prove that disproportionation occurred while the gases were still in contact with the solid sample, and that disproportionation is not caused by any external factor.

At higher temperatures, when the carbonate is partly decomposed, R decreases. This effect suggests that disproportionation is influenced by the pressure of carbon dioxide at the site of the reaction.

The applicability of the Prout and Tompkins equation means that the decomposition of the lanthanum oxalate is a branching chain reaction. A possible mechanism for these has been put forward by GLASNER and WEIDENFELD[11], namely that the gases stream out from the interior of the solid through channels, originating on the surface of the grains, and extend into the crystals as the reaction proceeds. The possible occlusion of gases in reactions of this type has recently been discussed by GAFNER[12]

It is most probable that in the channels mentioned above very high pressures of gas are built up, and disproportionation of the carbon monoxide occurs under the existing conditions. The observed decrease in R at temperatures at which the carbonate is unstable and carbon dioxide is evolved from an additional source, is thus a direct result of the mass action law.

The activation energy for the thermal decomposition of lanthanum oxalate is 31·7 kcal/mole oxalate (Table 2). The Ahrrenius plot (Fig. 6) of the induction periods t_0 indicates that what might be supposed to be the activation energy for the formation of new nuclei is higher, equalling 39·1 kcal/mole. Also the shift to the right in the reduced plot proves that the mechanism regulating the induction period is different from that of the main reaction. A difference of this nature, activation energies of the formation of nuclei being higher than for the main reaction, has often been observed. In the present case, some residual water present in the dehydrated oxalate is most probably responsible for the phenomenon. This is strongly indicated by our (yet unpublished) results with the other rare earth oxalates (see also ref. 2, TEREM). But it is also possible, that the induction period is at least partly due to the time necessary for the building up of a limiting pressure of gas in the channels.

[11] A. GLASNER and L. WEIDENFELD, *J. Amer. Chem. Soc.* **74**, 2467 (1952).
[12] G. GAFNER, *Trans. Faraday Soc.* **55**, 981 (1959).

J. Inorg. Nucl. Chem., 1961, Vol. 16, pp. 288 to 295. Pergamon Press Ltd. Printed in Northern Ireland

POLAROGRAPHIC BEHAVIOUR OF SOME PLATINUM(II) AND PALLADIUM(II) COMPLEXES

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Abstract—The polarographic behaviour of the *cis*- and *trans*-isomers of several platinum(II) and palladium(II) complexes has been studied in suitable supporting electrolytes. In all cases the reductions have been found to be irreversible. It has been observed that for all the diacido complexes the half-wave potential of the *trans* isomer is appreciably more negative than that of the *cis*.

IT is well known[1] that there exists a defininite relationship between the polarographic half-wave potential of a metal complex and its stability, the former becoming more negative with increasing magnitude of the latter. In agreement with this HOLTZCLAW[2a,c], and HOLTZCLAW and SHEETZ[2b] observed that in six co-ordinated complexes of cobalt(III) containing two acidic groups the *trans* isomer is reduced at a potential more negative than is the *cis*, the former being thermodynamically more stable. Platinum(II) and palladium(II) form a series of complexes which are known to exist in *cis*- and *trans*-forms. From the ease of conversion of a *cis* to the corresponding *trans* compound it appears that for palladium(II) the latter is more stable, as is generally true. However, platinum(II) compounds retain their configuration even under moderately drastic conditions, and nothing can be inferred from qualitative observations as to the relative stabilities of the isomeric forms. Kinetic studies indicate that in palladium(II) complexes[3] the *cis*-form is generally more reactive (labile) than the *trans*, while for platinum(II) complexes[4] the reverse is true, in keeping with the pronounced *trans-effect* phenomenon[5] which is exhibited. It is therefore of interest to investigate the relative stabilities of the *cis* and *trans* isomers of complexes of these two metals in their bipositive oxidation state. With this end in view the polarographic behaviour of several of their simple ammine complexes was investigated in potassium chloride or sodium perchlorate solution as supporting electrolyte, containing a little gelatin or methyl red (sodium salt) as maximum suppressor,

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EXPERIMENTAL

Apparatus. A Cambridge Pen-recording Polarograph was used to record the polarograms, using a cell with a dropping mercury electrode (D.M.E.) connected to an external saturated calomel electrode (S.C.E.) through and agar–potassium chloride bridge for all solutions containing potassium chloride, and an agar–sodium chloride bridge for those containing sodium perchlorate. In the apparatus used the cell resistance was ~600 Ω. Deaeration of the solution in the cell was effected by bubbling purified nitrogen through it before a run. The cell temperature was maintained constant (35·5 ± 0·1°C) by means of a water thermostat in which both the polarographic cell and the S.C.E.

[1] G. SARTORI, *J. Inorg. Nucl. Chem.* **8**, 196 (1958).
[2a] H. F. HOLTZCLAW, JR., *J. Amer. Chem. Soc.* **73**, 1821 (1951); [b] H. F. HOLTZCLAW, JR. and D. P. SHEETZ, *J. Amer. Chem. Soc.* **75**, 3053 (1953); [c] H. F. HOLTZCLAW, JR., *J. Phys. Chem.* **59**, 300 (1955).
[3] D. BANERJEA and K. K. TRIPATHI, *J. Inorg. Nucl. Chem.* **7**, 78 (1958).
[4] D. BANERJEA, F. BASOLO and R. G. PEARSON, *J. Amer. Chem. Soc.*, **79**, 4055 (1957).
[5] J. V. QUAGLIANO and L. SCHUBERT, *Chem. Rev.* **50**, 201 (1952).

were immersed. All potentials were recorded against the S.C.E. In most cases the half-wave potentials were evaluated from logarithmic plots and in a few cases directly from the polarograms.

Preparation of materials. *Cis-* and *trans*-$Pt(NH_3)_2Cl_2$, $Pt(en)Cl_2$, *trans*-$Pd(NH_3)_2Cl_2$, $Pd(en)Cl_2$, *cis-* and *trans*-$Pd(NH_3)_2(NO_2)_2$ (en = ethylenediamine) were prepared in a pure state by known methods.[3,4] Their purity was checked by analysis for metal and nitrogen:

Compound	Analysis, (%)			
	Found		Calcd.	
	Metal	Nitrogen	Metal	Nitrogen
Trans-$Pt(NH_3)_2Cl_2$	65·7	9·34	65·01	9·33
Cis-$Pt(NH_3)_2Cl_2$	65·2	9·43	65·01	9·33
$Pt(en)Cl_2$	59·3	8·81	59·82	8·58
Trans-$Pd(NH_3)_2Cl_2$	50·52	13·62	50·40	13·23
$Pd(en)Cl_2$	44·8	11·7	44·88	11·79
Trans-$Pd(NH_3)_2(NO_2)_2$	46·0	24·1	45·84	24·06
Cis-$Pd(NH_3)_2(NO_2)_2$	46·2	24·3	45·84	24·06

A fresh solution of each of these complexes was prepared, using the solid salt, in potassium chloride or sodium perchlorate solution, as required, and the maximum suppressor was then added. The polarogram was run immediately after making up the volume, thermostating the solution and deaerating with purified nitrogen. Aged solutions were prepared (without the maximum suppressor) by standing at 35·5 ± 0·1°C for the necessary period; the maximum suppressor was then added and the polarogram recorded after making up the volume.

Solutions of the diaquo complexes were prepared by treating the dichloro salts with the requisite quantity of silver perchlorate solution in the presence of sodium perchlorate and perchloric acid for ~½ hr on a water-bath for the platinum (II) compounds and at room temperature for about the same period in case of the palladium (II) compounds. The silver chloride which separated in each case was filtered off, and to the filtrate containing the perchlorate of the diaquo salt in sodium perchlorate and perchloric acid was added the requisite quantity of the maximum suppressor; the polarogram was then recorded after making up the volume.

The same procedure was employed for the dihydroxo complexes except that perchloric acid was absent during the precipitation of silver chloride; the requisite amount of sodium hydroxide solution was added to each of the filtrates, followed by the maximum suppressor before recording the polarogram.

RESULTS AND DISCUSSION

The polarograms are recorded in Figs. 1–6 and the half-wave potentials in Table 1. From the slopes of the plots of $-E_{D.M.E.}$ vs. $\log i/(i_d - i)$ it has been concluded that the electrode processes responsible for these waves are all irreversible.[6]

In the solutions of the dichloro salts of platinum(II) in 0·1 M potassium chloride there is only one wave and no change occurs on storing for a period of one day or more. Hence, under the above conditions even the two *cis*-compounds remain unchanged, although in aqueous solutions these change on standing to form the chloroaquo complexes to an appreciable extent.[4] This suggests that in 0·1 M potassium chloride the equilibrium in the system containing 0·5 mM of the complex

$$cis\text{-}PtB_2Cl_2 + H_2O \rightleftarrows cis\text{-}PtB_2(H_2O)Cl^+ + Cl^- \qquad \text{(i)}$$

(where $B_2 = 2NH_3$ or en)

[6] L. MEITES, *Polarographic Techniques* p. 104. Interscience, New York (1955).

favours almost 100 per cent of the dichloro salt. Although 0·005 per cent gelatin is sufficient to suppress the maximum in the wave of the *trans*-diammine, this is not so for the two *cis* compounds. Increasing the gelatin to 0·01 per cent eliminates the maximum in the wave of the ethylenediamine complex and almost eliminates that in

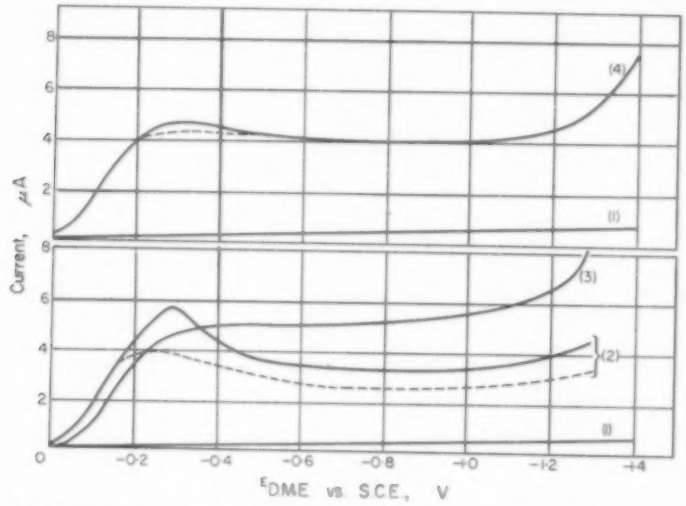

FIG. 1.—Polarograms of platinum(II) complexes in 0·1 potassium chloride containing gelatin (———, 0·005%; – – – –, 0·01%) Complex, 0·5 mM; *t*, 2·87 sec; *m*, 1·82 mg sec^{-1}; Temp. 35·5°C; (1) Blank; (2) *Cis*-$Pt(NH_3)_2Cl_2$; (3) *Trans*-$Pt(NH_3)_2Cl_2$; (4) $Pt(en)Cl_2$

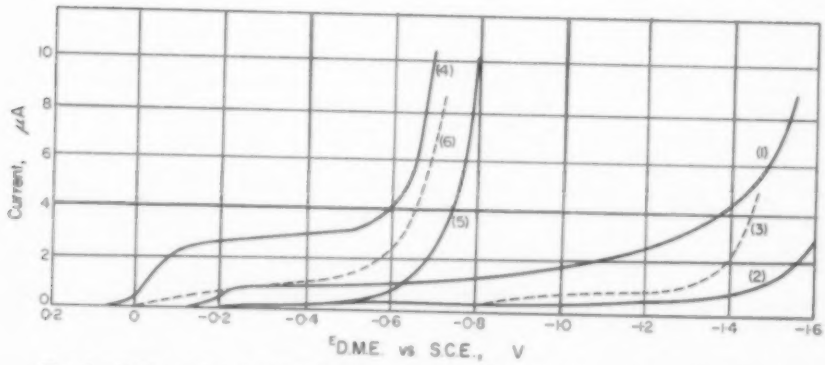

FIG. 2.—Polarograms of platinum(II) complexes in 0·1 M $NaClO_4$ containing 0·01 M NaOH (curves 1, 2 & 3) or 0·01 M $HClO_4$ (curves 4, 5 & 6) with 0·005% gelatin.
Complex, 0·5 mM; *t*, 2·9 sec; *m*, 1·85 mg sec^{-1}; Temp. 35·5°C
(1) *Trans*-$Pt(NH_3)_2(OH)_2$; (2) *Cis*-$Pt(NH_3)_2(OH)_2$; (3) $Pt(en)(OH)_2$; (4) *Trans*-$Pt(NH_3)_2(H_2O)_2^{2+}$; (5) *Cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$; (6) $Pt(en)(H_2O)_2^{2+}$
Blanks have not been shown, but are closely comparable with those of Fig. 6.

the wave of the *cis*-diammine. This makes an accurate determination of $E_{\frac{1}{2}}$ difficult. However, by taking the i_d value at −0·8 V vs. S.C.E., in the vicinity of which the current is independent of the potential, a fairly accurate value of $E_{\frac{1}{2}}$ could be obtained.

In the case of the diaquo and dihydroxo complexes of platinum(II) only the *trans*-diaquo compound has been found to give a clear wave while the rest apparently

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do not undergo any reaction. However, in all these cases, as in the case of the dichloro complexes, the final current rise occurs at a potential much less negative than the decomposition potential of the pure medium and is evidently due to the catalytic discharge of hydrogen ion.

In the case of the dichloro compounds of palladium(II) in 0·1 M potassium chloride it has been observed that a freshly-prepared solution of $Pd(en)Cl_2$ gives only

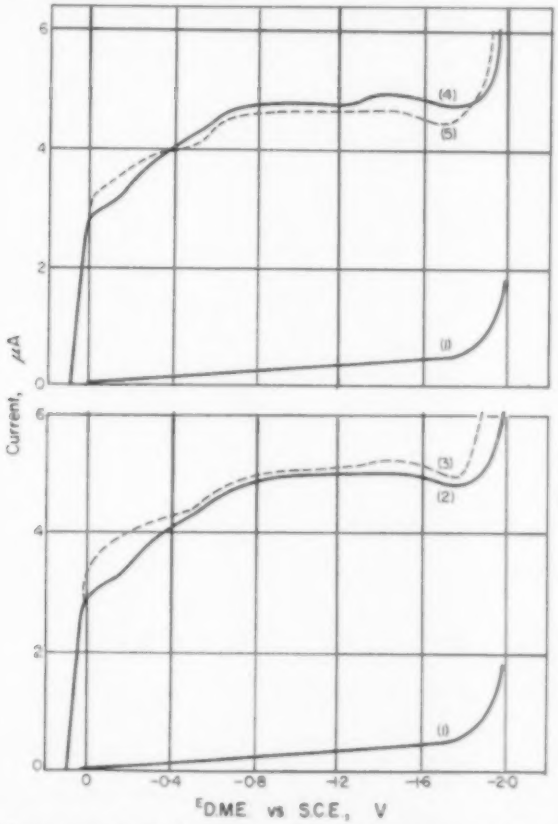

FIG. 3.—Polarograms of palladium(II) complexes in 0·1 M potassium chloride containing 0·0004% methyl red (sodium salt). Complex, 0·5 mM; t, 2·82 sec; m, 1·83 mg sec^{-1}; Temp. 35·5°C.
(1) Blank; (2) *Trans*-$Pd(NH_3)_2Cl_2$ (Fresh) (3) $Pd(en)Cl_2$ (Fresh); (4) *Trans*-$Pd(NH_3)_2Cl_2$ (Aged 24 hr); (5) $Pd(en)Cl_2$ (Aged 24 hr).

one wave with $E_{\frac{1}{2}} = -0{\cdot}585$ V vs. S.C.E. and no change occurs on storing the solution. However, a solution of the same compound and of the same concentration (0·5 mM) in 1 M potassium chloride, after being stored for two days, gives two waves with $E_{\frac{1}{2}}$ values of $-0{\cdot}63$ and $-1{\cdot}25$ V vs. S.C.E. It is already known[3] that in aqueous solution $Pd(en)Cl_2$ is rapidly and completely transformed into $[Pd(en)(H_2O)Cl]^+Cl^-$ and no further hydrolysis occurs to form the diaquo complex. On adding excess chloride ion the complex might be transformed into the dichloro compound, due to the equilibrium

$$Pd(en)Cl_2 + H_2O \rightleftarrows Pd(en)(H_2O)Cl^+ + Cl^- \qquad \text{(ii)}$$

Hence it appears that the first wave is due to the chloroaquo complex, while the second one is due to the dichloro compound. These results further indicate that the equilibrium constant of reaction (ii) is much higher than that of reaction (i), since even in 1 M potassium chloride the equilibrium in reaction (ii) is such that only incomplete conversion to the dichloro compound occurs.

FIG. 4.—Polarograms of palladium(II) complexes in 1 M potassium chloride containing 0·0004% methyl red (sodium salt).
Complex, 0·5 mM; t, 2·7 sec; m, 2·46 mg sec^{-1}; Temp., 35·5°C
(1) Blank; (2) *Trans*-$Pd(NH_3)_2Cl_2$ (Aged 48 hr); (3) $Pd(en)Cl_2$ (Aged 48 hr).

In the case of *trans*-$Pd(NH_3)_2Cl_2$ a freshly-prepared solution (0·5 mM) in 0·1 M potassium chloride gives two waves with $E_{\frac{1}{2}}$ values of −0·27 and −0·59 V vs. S.C.E. After storing for one day the same solution gives these waves and an additional one with $E_{\frac{1}{2}}$ of −1·32 V vs. S.C.E. In aged solutions in 1 M potassium chloride these three waves appear but with somewhat different $E_{\frac{1}{2}}$ values; the height of the third wave is, however, very much increased in this case, indicating a much greater concentration of the particular species which gives rise to this wave. It is known[3] that in aqueous solution *trans*-$Pd(NH_3)_2Cl_2$ is gradually and completely transformed into the diaquo complex via the chloroaquo complex which has been characterized. On adding

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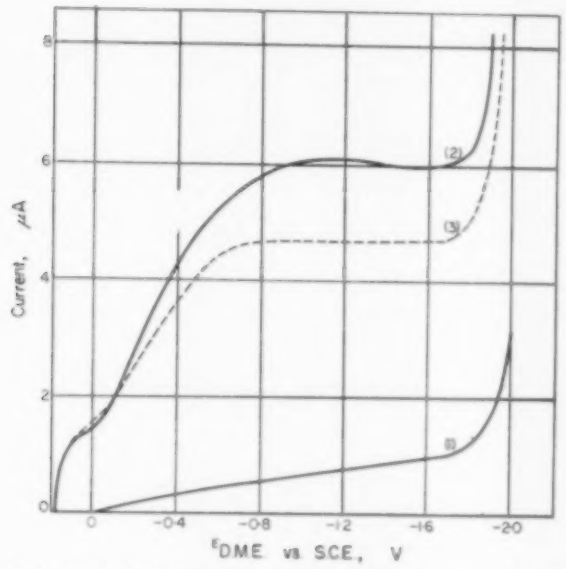

FIG. 5.—Polarograms of $Pd(NH_3)_2(NO_2)_2$ in 0·1 M $NaClO_4$ containing 0·0004 % methyl red (sodium salt).
Complex, 0·5 mM; t, 2·8 sec; m, 2·3 mg sec^{-1}; Temp. 35·5°C
(1) Blank; (2) *Trans*-isomer; (3) *Cis*-isomer.

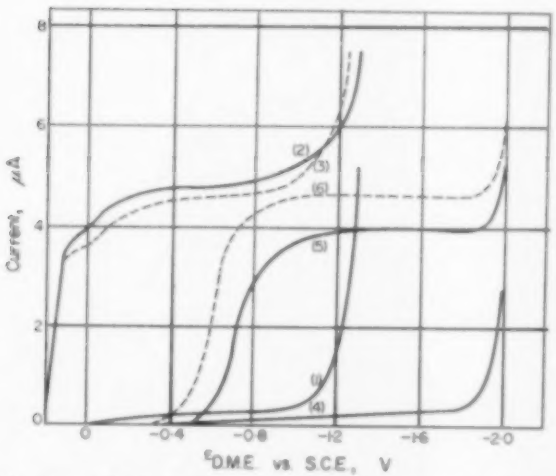

FIG. 6.—Polarograms of palladium(II) complexes in 0·1 M $NaClO_4$ containing 0·01 M $HClO_4$ (curves 1, 2 & 3) or 0·01 M NaOH (curves 4, 5 & 6) with 0·0004 % methyl red (sodium salt).
Complex, 0·5 mM; t, 3 sec; m, 2·32 mg sec^{-1}; Temp. 35·5°C
(1) & (4) Blank (2) *Trans*-$Pd(NH_3)_2(H_2O)_2^{2+}$; (3) $Pd(en)(H_2O)_2^{2+}$; (5) *Trans*-$Pd(NH_3)_2(OH)_2$
(6) $Pd(en)(OH)_2$.

TABLE 1.—HALF-WAVE POTENTIALS OF PLATINUM(II) AND PALLADIUM(II) COMPLEXES IN VARIOUS MEDIA

(Maximum suppressor: 0·005 per cent gelatin for Pt(II) and 0·0004 per cent methyl red (sodium salt) for Pd(II) compounds. Temp. 35·5 ± 0·1° C)

Complex (1)	Medium (2)	$E_{\frac{1}{2}}$ (V) (vs. S.C.E.) (3)	Remarks (4)
Trans-$Pt(NH_3)_2Cl_2$	0·1 M KCl	−0·165	—
Cis-$Pt(NH_3)_2Cl_2$	0·1 M KCl	−0·10	—
$Pt(en)Cl_2$	0·1 M KCl	−0·11	—
Trans-$Pt(NH_3)_2(OH)_2$	0·1 M $NaClO_4$ + 0·01 M NaOH	No reduction	—
Cis-$Pt(NH_3)_2(OH)_2$	0·1 M $NaClO_4$ + 0·01 M NaOH	No reduction	—
$Pt(en)(OH)_2$	0·1 M $NaClO_4$ + 0·01 M $HClO_4$	No reduction	—
Trans-$Pt(NH_3)_2(H_2O)_2^{2+}$	0·1 M $NaClO_4$ + 0·01 M $HClO_4$	ca. −0·05	—
Cis-$Pt(NH_3)_2(H_2O)_2^{2+}$	0·1 M $NaClO_4$ + 0·01 M $HClO_4$	No reduction	—
$Pt(en)(H_2O)_2^{2+}$	0·1 M $NaClO_4$ + 0·01 M $HClO_4$	No reduction	—
Trans-$Pd(NH_3)_2Cl_2$	0·1 M KCl (Fresh)	−0·27 −0·59	Diaquo complex Chloroaquo complex
$Pd(en)Cl_2$	0·1 M KCl (Fresh)	−0·585	Chloroaquo complex
Trans-$Pd(NH_3)_2Cl_2$	0·1 M KCl (Aged 24 hr)	−0·265 −0·585 −1·32	Diaquo complex Chloroaquo complex Dichloro complex
$Pd(en)Cl_2$	0·1 M KCl (Aged 24 hr)	−0·583	Chloroaquo complex
Trans-$Pd(NH_3)_2Cl_2$	1 M KCl (Aged 48 hr)	−0·237 −0·62 −1·37	Diaquo complex Chloroaquo complex Dichloro complex
$Pd(en)Cl_2$	1 M KCl (Aged 48 hr)	−0·63 −1·25	Chloroaquo complex Dichloro complex
Trans-$Pd(NH_3)_2(NO_2)_2$	0·1 M $NaClO_4$	−0·33	—
Cis-$Pd(NH_3)_2(NO_2)_2$	0·1 M $NaClO_4$	−0·27	—
Trans-$Pd(NH_3)_2(OH)_2$	0·1 M $NaClO_4$ + 0·01 M NaOH	−0·74	—
$Pd(en)(OH)_2$	0·1 M $NaClO_4$ + 0·01 M NaOH	−0·62	—
Trans-$Pd(NH_3)_2(H_2O)_2^{2+}$	0·1 M $NaClO_4$ + 0·01 M $HClO_4$	ca. −0·05	—
$Pd(en)(H_2O)_2^{2+}$	0·1 M $NaClO_4$ + 0·01 M $HClO_4$	ca. −0·06	—

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chloride ion, therefore, an equilibrium is slowly established between the three species

$$\begin{array}{l} \textit{trans}\text{-}Pd(NH_3)_2Cl_2 + 2H_2O \rightleftarrows \textit{trans}\text{-}Pd(NH_3)_2(H_2O)Cl^+ + Cl^- + H_2O \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow\uparrow \\ \qquad\qquad\qquad\qquad\qquad\qquad \textit{trans}\text{-}Pd(NH_3)_2(H_2O)_2^{2+} + 2Cl^- \end{array} \qquad \text{(iii)}$$

which give three waves,

In the palladium series, although *cis*-$Pd(NH_3)_2Cl_2$ has been described[7] the results obtained with ethylenediamine compound have been compared with those of the *trans*-diammine, as the ethylenediamine compound is well characterized and no conversion to the *trans*-structure is possible in this case, as might be the case with the *cis*-diammine because of the general lability of the *cis* structure in complexes of palladium(II). In a similar way the results on the corresponding diaquo and dihydroxo complexes have also been compared. However, in the platinum(II) series it has been shown here that the *cis*-diammine and the ethylenediamine complexes give almost identical $E_{\frac{1}{2}}$ values; they are also very similar in their kinetic behaviour.[4] The same might be expected to hold good in the palladium(II) series.

Both *cis*- and *trans*-$Pd(NH_3)_2(NO_2)_2$ in 0·1 M sodium perchlorate medium give one wave, $E_{\frac{1}{2}}$ for the latter being 60 mV more negative than that for the former. Solutions of all the palladium compounds studied in neutral or acid media give an initial current at zero volt (vs. S.C.E.) which precedes the normal reduction waves. This initial current is presumably due to formation of mercury(I) ions by reaction of the metal with the palladium(II) compounds.

From the values of $E_{\frac{1}{2}}$ given in Table 1 it may be observed that for all the platinum(II) and palladium(II) compounds containing two acidic groups (Cl^-, NO_2^-, OH^-) there is a significant difference ($\geqslant$60 mV) in the half-wave potentials of the *cis*- and *trans*- forms, $E_{\frac{1}{2}}$ being more negative for the latter. However, for the diaquo and chloroaquo complexes the values of $E_{\frac{1}{2}}$ are nearly identical (differing by not more than 10 mV). Thus the same general behaviour has been observed in the four-co-ordinated square planar complexes of platinum(II) and palladium(II) as in the six-co-ordinated octahedral complexes of cobalt(III). Hence, in spite of the differences observed in the kinetic behaviour of the isomeric complexes of platinum(II) and palladium(II), the *trans*-structure is thermodynamically more stable than the *cis* at least for the diacido complexes.

[7] A. A. Grinberg and V. M. Shulman, *Dokl. Akad. Nauk SSSR* 215 (1933); Cf. *Chem Abstr.* **28**, 1624 (1934).

J. Inorg. Nucl. Chem., 1961, Vol. 16, pp. 296 to 307. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES ON TTA COMPLEXES WITH METAL IONS—I

SPECTROPHOTOMETRIC AND POTENTIOMETRIC INVESTIGATIONS ON URANYL COMPLEXES

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Abstract—The nature and composition of the uranyl–TTA complex in an aqueous–alcoholic medium were investigated by spectrophotometric and potentiometric methods. The intensity of the colour of the complex is dependent on the pH and the alcoholic content of the medium. Spectrophotometric studies, which could only be extended to a maximum concentration of 1×10^{-4} M uranium, show that in dilute solutions the complex has the composition UO_2^{2+}:TTA = 2:3 whereas in concentrated solutions the potentiometric studies indicate that this ratio is 1:2. Chemical analysis of the solid complex also indicates a ratio of 1:2. A possible structure for the 2:3 complex has been proposed.

URANIUM is known to form a wide variety of complexes with organic reagents. During the last few years the complexes with β-diketones and their derivatives[1,2,3] have received considerable attention. Amongst these, thenoyl trifluoroacetone(TTA)

—CO—CH_2—CO—CF_3, has been extensively studied as a complexing agent for the separation of several metallic ions such as aluminium, beryllium, cobalt, copper, iron, zinc, yttrium, zirconium, actinium etc.[4–12] as it is highly stable in acidic media, insoluble in neutral and acidic aqueous solutions, and forms stable non-ionic chelates. Spectrophotometric investigations of the complexes of beryllium and other highly electropositive ions with TTA have been reported by BOLOMEY and WISH[13] and by ZEBROSKI[9]. WALTON *et al.*[3] have reported that uranium forms a complex of the type UO_2T_2 with TTA, the colour and composition of the solid varying according to the solvent from which it was obtained. They also mention that the ultra-violet spectrum of the complex in benzene was very variable and hence the nature of the complex could not be elucidated. It was found that the UO_2^{2+} complex with TTA was highly soluble in solvents such as acetone and alcohol and gave intensely-coloured solutions. This communication deals with spectrophotometric and potentiometric studies of the uranyl–TTA complex in an aqueous–alcoholic medium.

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EXPERIMENTAL

Reagents

Uranyl nitrate hexahydrate, absolute alcohol, KNO_3, and $NaClO_4$: all E. Merck's G.R. grade. TTA obtained from Dow Chemical Co. was used after recrystallisation from benzene.

Standard solutions of uranyl nitrate hexahydrate and of TTA (both 0·01 M), sodium perchlorate (0·5 M), and potassium nitrate (0·4 M) were prepared in 50 per cent alcohol and used after suitably adjusting the concentrations as required.

Apparatus

All extinction measurements were made with Beckman Du-spectrophotometer model 2400 using 10 mm Corex cells. Potentiometric studies were carried out using a Beckman pH-meter (model G) with a saturated calomel reference electrode and a glass electrode.

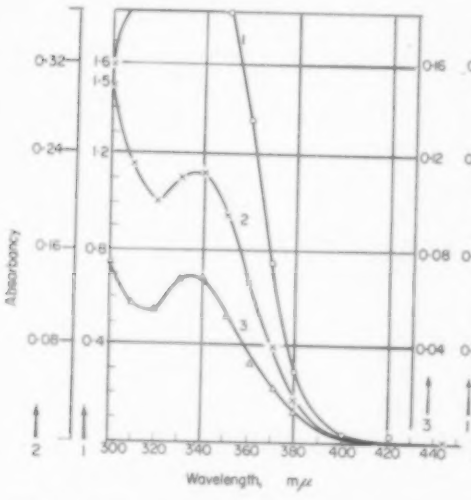

FIG. 1.—Spectra of TTA at varying concentration and constant pH (6·0) 1. 5×10^{-4} M; 2. 5×10^{-5} M; 3. 1×10^{-5} M.

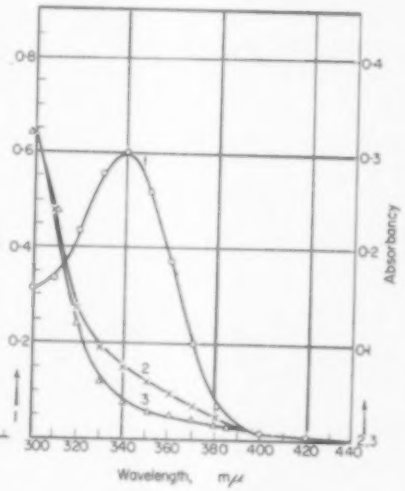

FIG. 2.—Spectra of TTA at varying pH and constant concentration (5×10^{-4} M) 1. pH = 6·9; 2. pH = 5·0; 3. pH = 3·1.

RESULTS

Absorption spectra of TTA, *uranyl nitrate and* TTA–*uranyl nitrate mixtures*

The absorption spectra of uranyl nitrate, TTA and uranyl nitrate–TTA mixtures, all in 50 per cent alcohol, were studied in the range 300–450 mμ. Figs. 1 and 2 give the absorption spectra of TTA as a function of concentration at constant pH and as a function of pH at a fixed concentration respectively. TTA shows a single absorption peak at 337 mμ which disappears at or below pH 5·0. No change with time was observed in the absorption peak, though such a change has been observed in solutions of TTA in benzene.[14] With increasing concentration of TTA the absorption increases enormously and for solutions above 1×10^{-4} M is beyond the measurable range. Fig. 3 shows the absorption spectra of uranyl nitrate and uranyl nitrate–TTA mixtures of varying composition. Two distinct absorption peaks at 337 mμ and 380 mμ are noticed in the spectra of uranyl nitrate–TTA mixtures and with increasing

[14] E. L. KING and W. H. REAS, *J. Amer. Chem. Soc.* **73**, 1806 (1951).

concentration of TTA in the mixture the peak at 337 mμ disappears. The absorption peak at 380 mμ is indicative of the formation of a uranyl–TTA complex in solution.

Effect of alcoholic content of the medium on the colour intensity

The alcohol content of the medium was found to have an appreciable effect on the intensity of the complex formed. This effect was studied by measuring the absorbancy of solutions of different alcoholic content (10–90 per cent), adjusted to constant pH (4·0) and containing uranyl ion and TTA in the constant ratio of 1:2. The results

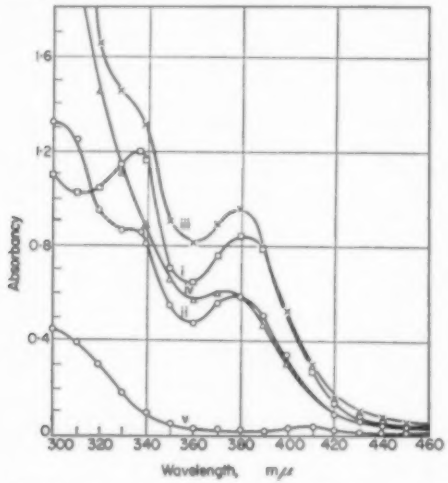

FIG. 3.—Spectra of mixtures of uranyl nitrate and TTA

	CONC. UO_2^{2+} (M)	CONC. TTA (M)	pH	UO_2^{2+}: TTA
i	5×10^{-4}	5×10^{-4}	4·85	1:2
ii	1×10^{-4}	5×10^{-4}	4·40	1:9
iii	5×10^{-4}	5×10^{-4}	4·55	1:45
iv	1×10^{-4}	5×10^{-4}	4·70	1:95
v	5×10^{-4}		3·4	

are given in Fig. 4. The absorbancy increased with the alcoholic content of the medium, the increase being more rapid in the range 10–50 per cent than at higher concentrations. As it was noticed that in solutions of low alcoholic content the colour of the solution faded gradually with time, 50 per cent alcoholic solutions were used for all further studies.

*Composition of the uranyl–*TTA *complex*

The composition of the complex was determined by (a) JOB's method of continuous variation[15,16] (b) molar ratio[17,18] and (c) slope ratio[17,19,20] methods.

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(a) *Job's method of continuous variation.* Equimolar solutions of uranyl nitrate and TTA ($2{\cdot}5 \times 10^{-4}$ M) in 50 per cent alcohol were mixed in various proportions at constant total molarity and pH and their absorbancies were measured at 337 and

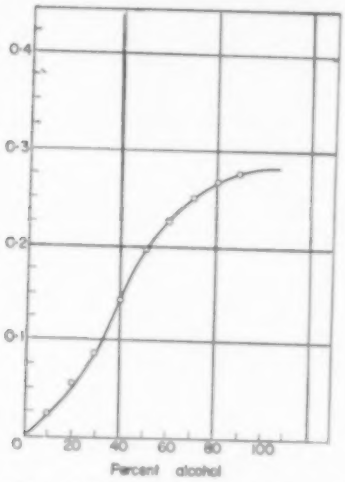

FIG. 4.—Effect of alcoholic content on the colour intensity.

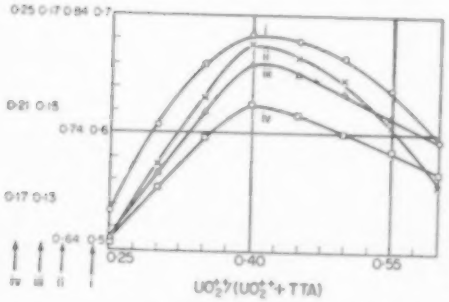

FIG. 5a.—Composition of UO_2^{2+} TTA complex by Jos's method

	mμ	pH
i	380	4·2
ii	337	4·2
iii	380	2·9
iv	337	2·9

Concentration of UO_2^{2+} and TTA solutions 2×10^{-4} M.

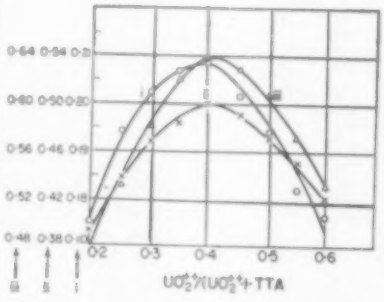

FIG. 5b.—Effect of varying the alcohol percentage on the composition of UO_2^{2+}:TTA complex, (i) 25%; (ii) 50%; (iii) 75%; Concentration of UO_2^{2+} and TTA solutions 5×10^{-5}M.

380 mμ. The plot of the difference between the observed extinction and the expected value if there were no reaction against composition is given in Fig. 5(a) for two sets of solutions adjusted to pH 2·9 and 4·2. It is seen that only one complex is formed, with the ratio UO_2^{2+}:TTA = 2:3. The same complex was found to be formed in 25 and 75 per cent alcoholic solutions also, as indicated by the curves in Fig. 5(b).

(b) *Molar ratio method.* Fig. 6 shows the effect of increasing the molar concentration of one of the reagents at a fixed concentration of the other (maintaining the pH of the solutions constant at 4·0), the absorbancy being measured at 380 mμ. The curves do not show any sharp break, indicating that the complex is highly dissociated.[18] The flattening of the curve was observed when the UO_2^{2+}:TTA ratio exceeded 1:8 (and 1:4 in the reverse case). This may also be due to the low percentage of the enol form of TTA present in the medium.[14] Experiments carried out at constant ionic strength in potassium nitrate or sodium perchlorate solution gave the same results.

(c) *Slope ratio method.* The composition of the complex was also determined by the slope ratio method. Two series of solutions were prepared by varying the concentration of one of the reagents in presence of a constant excess of the other. The pH of the solutions was adjusted to the same value (4·0) and their ionic strengths were maintained by the addition of potassium nitrate. The results of these experiments at ionic strengths 0·1 M and 0·01 M are given in Fig. 7. From the slopes the ratio of UO_2^{2+}:TTA were found to be respectively 1·62 and 1·54 at the two ionic strengths. These values are in good agreement with that obtained by JOB's method.

In the modified slope ratio method[19,20] the absorbancies of the solutions are plotted against the concentration of the variable components from either end of the x-axis. The point of intersection of the two curves corresponds to the composition of the complex, assuming that only one complex is formed. The result of such a plot is given in Fig. 8, and it is seen that the composition of the complex corresponds to UO_2^{2+}:TTA = 2:3.

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Effect of pH

It was noticed that in solutions below pH 2·5 and above 7·0 the colour of the complex was completely destroyed and hence the effect of pH on the colour intensity (i.e. extent of complex formation) was studied quantitatively.

Solutions of the reagents of concentration 5×10^{-4} M in 50 per cent alcohol were mixed in the ratio 2:3 (2 cm^3 uranyl nitrate + 3 cm^3 TTA), diluted to 15 cm^3 with 50 per cent alcohol and the pH approximately adjusted to values between 2 and 8 by adding dilute ammonia or nitric acid (also in 50 per cent alcohol). The volume of the solutions made up to 20 cm^3 and the pH measured accurately. The plot of the absorbancies of the solutions at 380 mμ against their pH values (curve 1, Fig. 9) shows that complex formation is a maximum at pH 6·0. Curve 2 in Fig. 9 shows the variation in the absorbancy of the complex with the pH of the solution when a large excess of TTA is used. The increase in the absorbancy above pH 6·0 (curve 2) is due to the excess TTA in solution.

Preparation of the UO_2T_2 *complex and its absorption spectra in solution*

Since no evidence for the formation of a 1:2 complex was obtained in solution, it was considered worth while to study the absorption spectra of solid UO_2T_2 dissolved in 50 per cent alcohol. The UO_2T_2 complex was prepared as follows:

Uranyl nitrate hexahydrate and 0·1 M TTA solutions in absolute alcohol were mixed in the ratio 1·2:2·0 (to ensure excess of uranium in solution) and the solid UO_2T_2 was precipitated by diluting with water. The yellow precipitate was filtered and washed free of excess uranium with distilled water. It was then dried to constant

weight over calcium chloride in a desiccator at room temperature. The colour of the precipitate changed gradually from yellow to orange-red during these operations.

The analysis of the solid complex conformed to the formula $UO_2T_2{\cdot}2H_2O$.

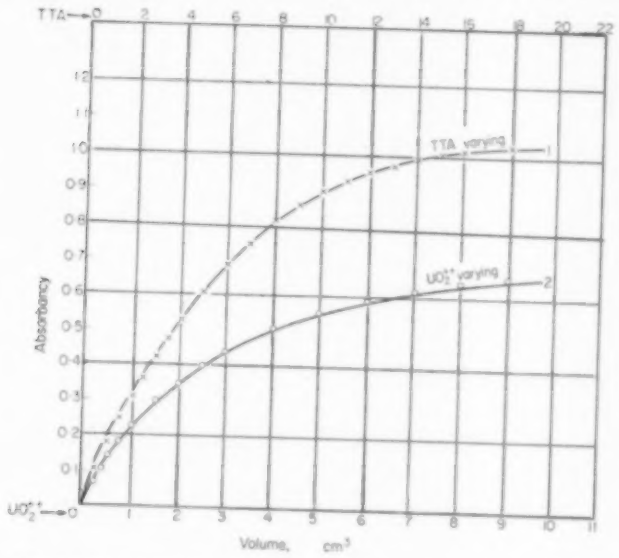

FIG. 6.—Composition by molar ratio method. (1) 2 cm³ 5×10^{-4} UO_2^{2+} vs. 5×10^{-4} M TTA. (2) 2 cm³ 5×10^{-4} TTA vs. 5×10^{-4} M UO_2^{2+}. Ionic strength 0·1 M in $NaClO_4$.

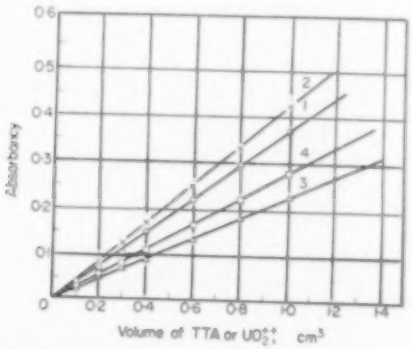

FIG. 7.—Composition of UO_2^{2+} TTA complex by slope ratio method. (1) TTA 10 cm³ $2{\cdot}5 \times 10^{-4}$ M (FIXED), $\mu = 0{\cdot}1$ M; (2) TTA 10 cm³ $2{\cdot}5 \times 10^{-4}$ M (FIXED), $\mu = 0{\cdot}01$ M; (3) UO_2^{2+} 10 cm³ $2{\cdot}5 \times 10^{-4}$ M, $\mu = 0{\cdot}1$ M; (4) 10 cm³ $2{\cdot}5 \times 10^{-4}$ M, $\mu = 0{\cdot}01$ M.

The absorption spectra of $UO_2T_2{\cdot}2H_2O$ and of the 2:3 complex formed directly in solution in 50 per cent alcohol at varying pH are given in Figs. 10 and 11. In both cases the absorption spectra are identical, with maxima at 337 and 380 mμ. This indicates that $UO_2T_2{\cdot}2H_2O$ in solution in 50 per cent alcohol exists as a 2:3 complex. With decreasing pH the intensities of the peaks at 337 and 380 mμ diminish, and at about pH 2·5 both peaks disappear simultaneously. With increasing pH above 6·0 the intensity of the 337 mμ peak increases greatly compared with that at 380 mμ.

The absorption spectra of $UO_2T_2 \cdot 2H_2O$ in 50 per cent alcohol at different concentrations show that the concentration of the complex has no effect on the nature of the spectrum in the range investigated ($6{\cdot}6 \times 10^{-6}$ M to $3{\cdot}3 \times 10^{-5}$ M). The

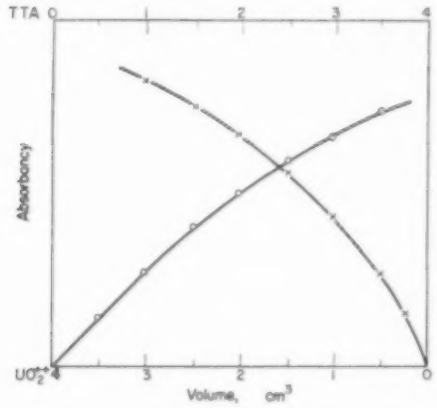

FIG. 8.—Composition of UO_2^{2+} TTA complex by slope ratio method. Volume of UO_2^{2+} and TTA taken = 3 cm³ each of 5×10^{-4} M.

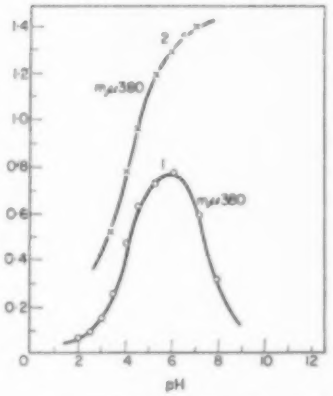

FIG. 9.—Effect of pH. (1) 2 cm³ UO_2^{2+} + 3 cm³ TTA 5×10^{-4} M each. (2) 1 cm³ UO_2^{2+} + 9 cm³ TTA 1×10^{-4} M, 5×10^{-4} M respectively.

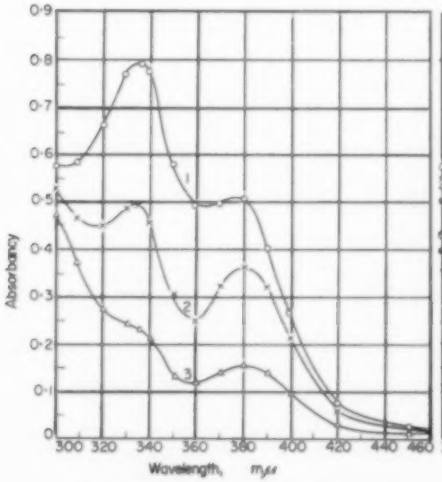

FIG. 10.—Spectra of solid UO_2T_2 complex. (4·5 mg/100 cm³) in 50% alcohol. (1) pH 6·75; (2) pH 4·8; (3) pH 3·7.

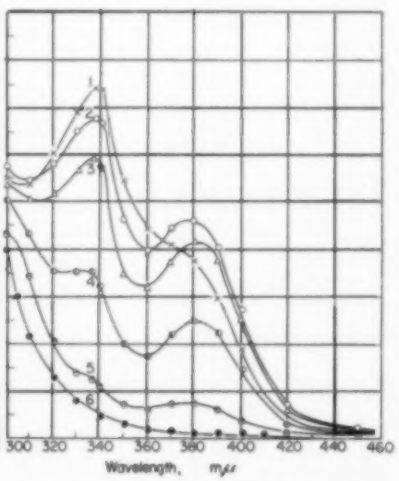

FIG. 11.—Spectra of UO_2–TTA complex (2:3) in 50 per cent alcohol. (1) pH 7·0; (2) pH 6·0; (3) pH 4·85; (4) pH 3·99; (5) pH 3·15; (6) pH 2·5.

absorption spectra of the solid complex in benzene is also similar to that in 50 per cent alcohol (Figs. 12, 10). TTA, however, does not give an absorption peak in benzene when the solution is freshly prepared (curve 2, Fig. 12) and the spectral behaviour of the $UO_2T_2 \cdot 2H_2O$ complex and TTA in benzene are discussed later.

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*Formation constant of the uranyl–*TTA *complex formed in solution*

The formation constant of the uranyl–TTA complex in solution was determined according to the method of TANAKA and TAKAMURA[21]. When a, the total concentration of UO_2^{2+}, is in a large excess over b, the total concentration of TTA, the concentration of the complex formed in solution, c, can be expressed by the equation

$$c = k(a - 2c)(b - 3c) = kab/(1 + 3ak) \tag{1}$$

where k is the formation constant of the species in solution expressed in terms of molar concentration.

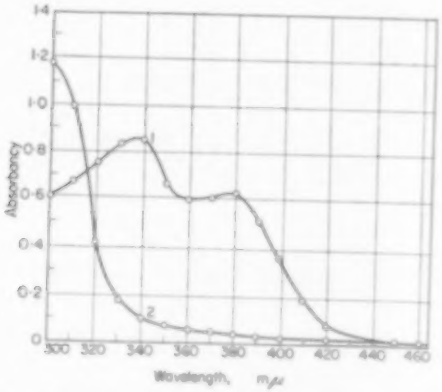

FIG. 12.—Spectra of: (1) Solid complex ($UO_2T_2 \cdot 2H_2O$) dissolved in benzene ($6{\cdot}6 \times 10^{-5}$ M) (2) TTA in benzene (2×10^{-5} M)

If Beer's law is obeyed, the absorbancy D is given by

$$D = \varepsilon c = \varepsilon kab/(1 + 3ak) \tag{2}$$

or

$$\frac{ab}{D} = \frac{3a}{\varepsilon} + \frac{1}{\varepsilon k} \tag{3}$$

where ε is the molar extinction coefficient of the complex. By plotting ab/D against a, a linear relationship is obtained, and from the values of the slope of the line and its intercept k and ε can be determined (Fig. 13).

Extinction measurements for UO_2^{2+}–TTA mixtures at constant ionic strengths of 0·1 and 0·01 M in KNO_3 made by varying the concentrations of UO_2^{2+} and TTA up to $2{\cdot}5 \times 10^{-5}$ M in presence of a fixed higher concentration of TTA and UO_2^{2+} ($2{\cdot}5 \times 10^{-4}$ M) respectively, show that Beer's law is obeyed under these experimental conditions (Fig. 7). Another set of experiments was carried out by varying the concentration of UO_2^{2+} from $3{\cdot}75 \times 10^{-5}$ M up to $2{\cdot}5 \times 10^{-4}$ M in presence of a low fixed concentration of TTA ($12{\cdot}5 \times 10^{-6}$ M) and measuring the absorbancies of the solutions adjusted to a constant pH (4·0) at 380 mμ. The results are given in Table 1 and the values of ab/D are plotted against the concentration of UO_2^{2+}, (a), in Fig. 13.

[21] N. TANAKA and T. TAKAMURA, *J. Inorg. Nucl. Chem.* **9**, 15 (1959).

TABLE 1.—ABSORPTION MEASUREMENTS FOR DETERMINATION OF THE FORMATION CONSTANT OF THE URANYL–TTA COMPLEX*

Conc. of UO_2^{2+} ($\times 10^{-5}$ M) a	D observed		$(ab/D) \times 10^{-5}$	
	$\mu = 0{\cdot}1$	$\mu = 0{\cdot}01$	$\mu = 0{\cdot}1$	$\mu = 0{\cdot}01$
3·75	0·095	0·080	4·92	5·86
7·50	0·115	0·102	8·15	9·19
10·00	0·118	0·111	10·60	11·20
12·50	0·122	0·117	12·80	13·30
15·00	0·127	0·122	14·70	15·37
20·00	0·130	0·130	19·20	19·20
25·00	0·132	0·131	23·60	24·00

* $b = 1{\cdot}25 \times 10^{-6}$ M. μ = ionic strength of the solution in M.

The calculated values of K from the above readings were $2{\cdot}5 \times 10^4$ and $1{\cdot}10 \times 10^4$ at $\mu = 0{\cdot}1$ and 0·01 M respectively.

Analytical application

The suitability of the highly-coloured uranyl–TTA complex in alcoholic solution for the colorimetric estimation of small amounts of uranium was investigated.

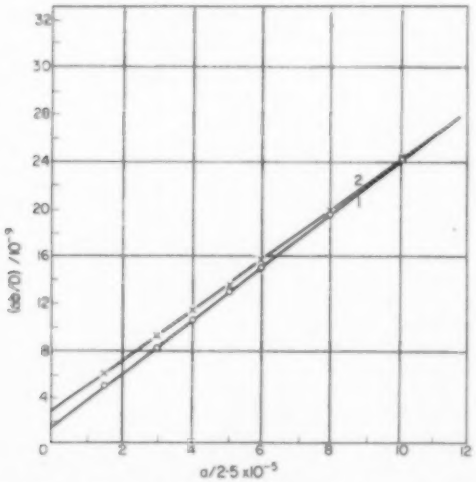

FIG. 13.—Plot of ab/D vs. a. (1) $\mu = 0{\cdot}1$ M; (2) $\mu = 0{\cdot}01$ M.

(a) *Verification of Beer's law.* It has already been seen that Beer's law is obeyed in the range 0–25 p.p.m. at pH 4·0 (Fig. 7, curves 1 and 2). Experiments were repeated to test the applicability of Beer's law at pH 6·0 (the optimum value for maximum colour intensity) in solutions of varying alcohol concentration. It was observed that Beer's law is obeyed in 25, 50 and 75 per cent alcohol solutions at 380 mμ in the range 1–50 p.p.m. of uranium. The sensitivity increases however with the alcohol content of the medium.

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(b) *Stability of the complex.* The colour of the complex was found to be very stable and its intensity did not change even after 72 hr in solutions containing 50 per cent alcohol and above. In solutions containing 25 per cent alcohol and below the colour faded gradually with time.

(c) *Interfering ions.* The effect of a number of ions such as Ti^{4+}, Fe^{3+}, Ce^{4+}, Be^{2+}, Cu^{2+}, PO_4^{3-}, SO_4^{2-}, MoO_4^{2-}, Cl^- and NO_3^- was investigated. It was found that all except Cl^- and NO_3^- interfered in the estimation.

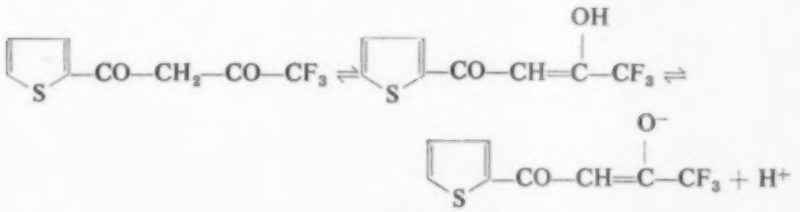
Potentiometric studies

The nature of the uranyl–TTA complex was also investigated by carrying out potentiometric titrations of uranyl nitrate–TTA mixtures in 50 per cent alcohol with ammonia, keeping the ionic strengths of all reagents constant at 0·1 M with KNO_3. The results are given in Fig. 14.

Curve 1 refers to TTA alone, curve 2 to uranyl nitrate and curves 3–6 to uranyl nitrate–TTA mixtures with ratios of UO_2^{2+}:TTA equal to 1:1, 2:3, 1:2 and 1:4. Curves 3 and 4 show two breaks, the first at 1 and 1·5 equivalents of ammonia and the second at 2·3 and 2·2 equivalents of ammonia respectively. The second break in the two curves agrees with the value for uranyl nitrate alone (2·3 equivalents). Curves 5 and 6 also show breaks at approximately 2·3 equivalents corresponding to the second break in curves 3 and 4. The latter part of curve 6 represents the neutralisation of excess TTA.

DISCUSSION

The following equilibria exist in solutions of thenoyl trifluoroacetone (TTA).



The absorption spectrum of TTA (Fig. 1) shows a maximum at 337 mμ due to its enolic form in accordance with the observations of SACCONI and GIANNONI[2], who observed that β-diketones gave an absorption maximum in the range 307–349 mμ. In solutions of low pH the enolisation of TTA is suppressed, as seen in the curves in Fig. 2, where the 337 mμ peak disappears below pH 5·0. The spectrum of freshly-prepared solutions of TTA in benzene (Fig. 13, curve 2) is similar to that reported by KING and REAS[14].

As already mentioned, uranyl nitrate–TTA mixtures show an absorption peak at 380 mμ (Fig. 3) in addition to the 337 mμ peak, which is also in agreement with observations of the above-mentioned authors on the uranyl complexes of β-diketones (376–403 mμ).

All the spectrophotometric methods employed to determine the composition of the uranyl–TTA complex in dilute solutions show the formation of a 2:3 complex which may be formulated as a bridged complex with the structure shown below. The behaviour of hydroxide groups to form olated compounds is well known, and

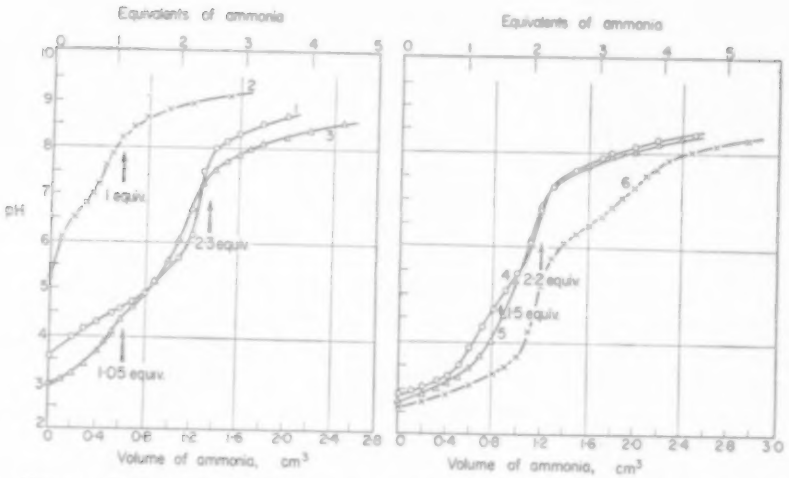
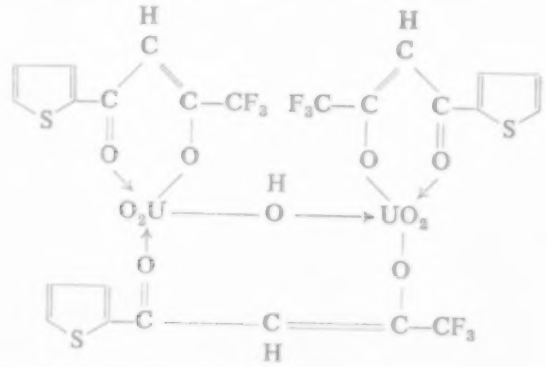


FIG. 14.—Electrometric titration curves. (1) 20 cm³ of $2{\cdot}5 \times 10^{-3}$ M UO_2^{2+}; (2) 20 cm³ of $2{\cdot}5 \times 10^{-3}$ M TTA; (3) 20 cm³ of $UO_2^{2+} + 2{\cdot}5 \times 10^{-3}$ M TTA (Ratio 1:1); (4) 20 cm³ of $2{\cdot}5 \times 10^{-3}$ M $UO_2^{2+} + 3{\cdot}75 \times 10^{-3}$ M TTA (Ratio 1:1·5); (5) 20 cm³ of $2{\cdot}5 \times 10^{-3}$ M $UO_2^{2+} + 5 \times 10^{-3}$ M TTA (Ratio 1:2); (6) 20 cm³ of $2{\cdot}5 \times 10^{-3}$ M $UO_2^{2+} + 1 \times 10^{-2}$, TTA (Ratio 1:4).

potentiometric studies of the hydrolysis of U^{6+}, Bi^{3+}, Cu^{2+} and Sc^{2+} indicate that the formation of bridged compounds may be a general phenomenon.[21–25] The stability of the colour of the complex in solution and the high pH at which it shows maximum intensity indicate the possibility of an 'ol' bridged compound.



In this structure the valency of uranium(VI) is satisfied and the UO_2^{2+} ion can have the maximum co-ordination number six if there are two solvent molecules attached to it. The formation of an eight-membered ring by OH bridging between the two UO_2^{2+} groups shows that the complex should be highly-dissociated in solution. This is corroborated by the low formation constant of the complex.

The solid uranyl–TTA complex corresponds to the formula $UO_2T_2{\cdot}2H_2O$ and it

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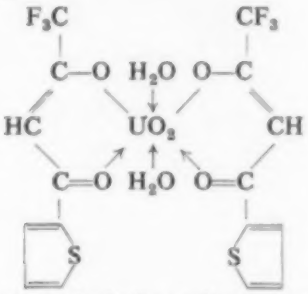
can be represented as follows:



In dilute solution in an aqueous–alcoholic medium the solid complex may undergo a transformation as follows:

$$2(UO_2T_2{\cdot}2H_2O) \rightarrow (UO_2)_2T_3OH + HT + 3H_2O$$

The similarity in the absorption spectra of the 2:3 complex and of the solid complex in dilute solution in 50 per cent alcohol (Figs. 11 and 10) supports the assumption of such a transformation. While in TTA alone the 337 mμ peak due to the enolic form of TTA is suppressed below pH 5·0, in the spectrum of the complex this peak appears even at pH 2·5. Hence the peak at 337 mμ in the spectrum of the complex below pH 5·0 can be attributed to the enolic form of TTA bound with UO_2^{2+} in the complex, which cannot be destroyed up to pH 2·5. This is evident from the curves in Fig. 11, which show that the complex exists between pH 2·5 and 7, as indicated by the disappearance of the 337 mμ and 380 mμ peaks in curve 6 and of the 380 mμ peak in curve 1.

The formation of a 2:3 complex in dilute aqueous–alcoholic solutions from solid $UO_2T_2{\cdot}2H_2O$ raises the question whether in the solid state also $UO_2T_2{\cdot}2H_2O$ exists as $[(UO_2)_2T_3OH{\cdot}HT{\cdot}3H_2O]$. This cannot be established by the present study, and it can only be inferred that uranium (VI) forms with TTA a 1:2 complex in the solid state and a 2:3 complex in dilute aqueous–alcoholic solutions.

The complex formation between UO_2^{2+} and TTA in aqueous–alcoholic solutions and the high stability of the colour of the complex can be advantageously used for the spectrophotometric determination of small amounts of uranium even down to 1 p.p.m. The pH of the solution must be carefully adjusted, since the intensity is appreciably influenced by it (Fig. 9). The sensitivity of the method increases with the alcoholic content of the medium. Considering the high complexing capacity of TTA it would be expected that most ions would interfere in the estimation of uranium, and the effect of several ions which were investigated showed that it was necessary to separate uranium from such ions before estimation. Thus, for quantitative estimation of uranium the pH, alcohol content of the solution, the amount of TTA, and the presence of foreign ions should be carefully controlled.

The results of potentiometric titrations give no indication of the formation of a 2:3 complex in concentrated solutions ($\gtrsim 2{\cdot}5 \times 10^{-3}$ M) but all show the presence of a 1:2 complex irrespective of the UO_2^{2+}:TTA ratio in solution. Hence it is concluded that in concentrated solutions, as in the solid state, uranium exists as a 1:2 complex, and in very dilute solutions as a 2:3 complex with TTA.

Acknowledgements—The authors wish to thank Dr. J. SHANKAR for his keen interest in the work and Dr. A. R. GUPTA for his helpful comments.

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EXTRACTION EQUILIBRIA IN THE SYSTEM AQUEOUS HYDROCHLORIC ACID–URANYL CHLORIDE–TRI-N-BUTYL PHOSPHATE

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Abstract—The distribution of uranyl chloride between aqueous hydrochloric acid solutions and undiluted tri-n-butyl phosphate (TBP) was examined as a function of increasing acid concentration in the initial aqueous solution, the metal concentration being kept constant, and as a function of increasing uranyl chloride concentration for constant acid content of the initial aqueous solution. The pregnant organic layers involved were investigated by means of volume-swelling determinations, and by viscosity, density, conductivity and spectrophotometric measurements. The water content of the tri-butyl phosphate layer was also determined.

It was found that the chemical mechanism governing the extraction of uranyl chloride is largely dependent upon the hydrochloric acid concentration in the initial aqueous solutions. For low acid concentrations the mutual salting-out effect of the two solutes controls the mechanism; at medium acid concentrations (1–7 M HCl) the acid concentration has no marked influence on the extraction mechanism involved; at high acid concentrations it is the competition between two complex-solvates, namely the hydrochloric acid-monosolvate-trihydrate and the uranyl chloride-disolvate, which controls the extraction of uranyl chloride from aqueous solutions.

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A SUBSTANTIAL proportion of the investigations on the extraction of uranium by TBP have been concerned with solutions of the metal nitrate in nitric acid solutions.[1] Although it has been shown[2–10] that uranium can also be extracted from hydrochloric acid by TBP, little information can be found in the literature on the mechanism of the extraction. The chemical mechanism involved was believed to be similar to that existing in the system containing uranium nitrate and nitric acid, viz

$$UO^{2+}_{2(a)} + 2NO^{-}_{3(a)} + 2TBP_{(o)} \rightarrow [UO_2(NO_3)_2 \cdot 2TBP]_{(o)}.$$

Despite its experimental simplicity, the solvent extraction of metallic salts from aqueous solution is a theoretically complex process of heterogeneous equilibrium, as the tendency for a given element to be extracted from an aqueous into an organic phase is largely dependent upon the anion accompanying the metal, and is even more dependent upon the hydration of the electrolyte in the organic phase. In our

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investigation, special emphasis was placed on the important rôle which water plays in the extraction of electrolytes into TBP[11]. Therefore, in view of the fundamental differences in the extraction by TBP of nitric and hydrochloric acids, pointed out in previous studies from this [12,13]and other laboratories[2], it was felt that the mechanism of extraction of uranium(VI) from hydrochloric acid solutions must differ from the above chemical mechanism for uranyl nitrate extraction from nitric acid media. The high water content taken up by TBP during the extraction of hydrochloric acid is primarily responsible for these differences. It is the purpose of the paper to propose a chemical mechanism for the tributyl phosphate extraction of uranyl chloride from aqueous solutions containing varying concentrations of the solutes, and to test this by a quantitative analysis of physical–chemical data[12,14,15] pertaining to the system.

EXPERIMENTAL

Baker's "Analysed Reagents" grade hydrochloric acid and May & Baker's uranium chloride were used in these experiments; no further purification of the uranium salt was found to be necessary. Tri-n-butyl phosphate, obtained from Commercial Solvents Corporation, was purified by washing with sodium hydroxide solution and then six times with distilled water. The dissolved water was removed by distillation[16,17].

The initial aqueous solutions were prepared by mixing calculated amounts of stock solutions, both hydrochloric acid and uranyl chloride, with distilled water to give the appropriate initial concentrations. The concentrated uranium solution was prepared by dissolving uranium chloride in distilled water and saturating the solution obtained with hydrogen chloride at room temperature. The resulting solution contained 3·21 M uranyl chloride and 8·83 M hydrochloric acid. Undiluted TBP was used as extractant throughout these experiments.

Equilibrium and volume change measurements were carried out by introducing 5 ml of both aqueous solution and TBP into 10 ml graduated centrifuge tubes, as described previously[12,15]. It was shown by separate experiments that 15 min mixing periods were sufficient to establish equilibrium in both the high-uranium and low-uranium studies. The laboratory temperature varied between 18 and 22°. The effect of temperature within this range was shown to be within the error of the determinations.

Absorption spectra were measured with a Beckman Model DU spectrophotometer with 1 cm glass cells, and when necessary glass spacers were employed. Determinations of the physical–chemical data, the density, viscosity and conductivity of the homogeneous organic layers, were performed immediately after equilibration and separation, as described in a previous paper.[12] The uranium content was determined either colorimetrically by the thiocyanate method[18] or gravimetrically by the 8-hydroxyquinoline procedure.[19] Only the aqueous phase was analysed, the uranium content of the other phase being obtained by difference from the total uranium content. In several cases, a test for material balance was made. The results showed that for extraction ratios between 0·2 and 100, reproducibility was better than ± 4 per cent at low uranium and ± 1 per cent at high uranium content experiments. The concentration of the acid in the samples with high uranium content was calculated from the results of chloride titrations by the Volhard method, by subtracting twice the uranium concentration from the chloride value. Water determinations in the TBP layers were carried out by means of Karl Fischer reagent.[12]

Since the instability of tributyl phosphate solutions of uranyl chloride in the presence of hydrochloric acid was repeatedly confirmed, all solvent equilibrations were made immediately prior to use.

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[19] A. I. Vogel, *Quantitative Inorganic Analysis*. Longmans, Green, London (1958).

Such solutions display a rather rapid change, the uranium(VI) being photolytically reduced to uranium-(IV) and the TBP hydrolysed to alkyl phosphates, resulting in a greenish precipitate. New data on the hydrolytic degradation of TBP in the presence of hydrochloric acid and on the phenomena mentioned above, were recently obtained in this laboratory and will be reported in a subsequent publication; discussion of the results in connection with the system under consideration will therefore be deferred.

RESULTS

Two series of experiments were carried out. The first related to the variation of the extraction ratio, E_a^o, of uranium(VI) as a function of the initial hydrochloric acid concentration for a constant concentration of uranyl chloride (0·092 M) in the initial aqueous solution, this being the original concentration in the aqueous phase before any partition of the solutes between the two phases. The second set of experiments, designed to study more precisely the heterogeneous equilibrium involved during the passage of the two solutes into the organic layer, consisted of physical–chemical and distribution studies under conditions of constant acidity and varying concentrations of uranyl chloride in the initial aqueous solutions. The aqueous electrolyte concentration in this set of experiments was chosen to be near to saturation.

Studies with low uranium content

In the ternary system H_2O–HCl–TBP, the basic system for that under consideration, a number of interactions between the components were detected by a physical–chemical analysis of the pregnant organic layers.[12] If, when dealing with the extraction of an inorganic salt from hydrochloric acid, the restriction $C_M \ll C_{HCl}$ is applied, the behaviour of the system as a whole should not differ significantly from that of the simpler two-phase condensed system of three components, viz., water–hydrochloric acid–tributyl phosphate. The behaviour of this basic system—at least as far as changes in phase ratios and solvent properties are concerned—will serve as a common pattern for the extraction of any metal. Some information on the above is derived from a previous study of the distribution of heptavalent rhenium between nitric acid and tributyl phosphate[20] and further evidence is presented in this study. The concentration of $9{\cdot}2 \times 10^{-2}$ M uranyl chloride is sufficiently low so as not to modify the phase isotherms. The extent of mutual miscibility of the phases, the density, viscosity and conductivity of the organic phases, and the distribution of hydrochloric acid between water and TBP seem to be unaffected by the presence of the low uranium content in the system, except for the distribution at low acid concentrations below 1 M. Figs. 1 and 2 show respectively the distribution of the acid between the two phases and the viscosities of the organic layers, both in the presence and in the absence of uranyl chloride. Table 1 shows that the presence of uranium influences neither the mutual solubility of the phases nor the high content of water taken up by TBP during the extraction of HCl. Density and conductivity measurements also give substantially the same values for both systems.

Table 1 shows further the variation of the extraction ratio of uranium from aqueous solution by an equal volume of the solvent. The number of chloride atoms in the extracted complex was deduced conventionally from the slope of a log-log plot of the extraction ratio versus the ligand activity[21] in the equilibrium aqueous phase, for constant uranium concentration in the initial aqueous solution and constant extractant

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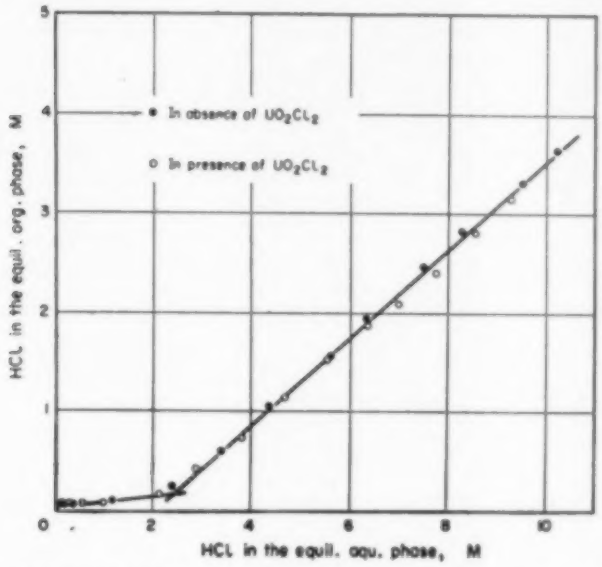

FIG. 1.—Distribution of HCl between water and 100% TBP in the presence and in the absence of 0·092 M UO_2Cl_2.

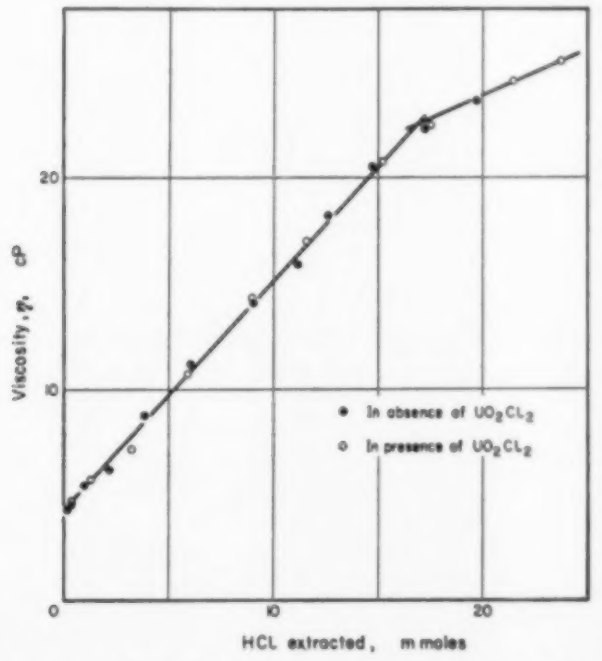

FIG. 2.—Viscosity of the equilibrium organic phases as a function of their HCl content, in the presence and in the absence of 0·092 M UO_2Cl_2.

concentration in the organic phase, as shown in Fig. 3. The extraction ratio for uranium is shown to vary as the second power of the aqueous chloride activity over a wide range, suggesting a molar chloride to metal ratio of two in the extracted species. The distribution isotherm (Fig. 3) shows a maximum extraction ratio for concentrations of acid in the initial aqueous solution of about 7 M, in accordance with previous findings[2,4,9]. An explanation for this phenomenon will be proposed later on, when the extraction mechanism is discussed. At low acid concentrations, up to about 1 M

TABLE 1.—THE DISTRIBUTION OF 0·092 M UO_2Cl_2 AND HCl BETWEEN WATER AND UNDILUTED TBP AS A FUNCTION OF THE ACID CONCENTRATION IN THE INITIAL AQUEOUS SOLUTION. PHASE VOLUMES 5 ml (18·35 MMOLES TBP).

No. of Exp.	HCl (M)		UO_2Cl_2, (M) Equil. aq. phase	Swelling of the organic phase V, (ml)	$E^{\circ}_{a_{UO_2Cl_2}}$	Extracted into the organic phase, (mmole)		
	Init. aq. soln.	Equil. aq. phase				acid	uranium	water
1	2	3	4	5	6	7	8	9
1	—	—	—	0·30	—	—	0·00	18·2
2	0·14	0·14	0·096	0·30	0·02	0·04	0·01	18·3
3	0·28	0·25	0·082	0·30	0·17	0·21	0·07	17·9
4	0·57	0·54	0·080	0·30	0·20	0·28	0·09	18·4
5	1·07	1·06	0·072	0·30	0·31	0·36	0·12	18·6
6	2·11	2·06	0·040	0·30	1·26	0·87	0·27	19·7
7	3·16	2·94	0·017	0·40	4·34	2·18	0·39	24·3
8	4·21	3·85	0·009	0·60	8·95	3·88	0·46	34·7
9	5·29	4·71	0·003	0·75	24·1	6·00	0·46	42·1
10	6·30	5·48	0·002	0·90	48·9	9·05	0·46	50·7
11	7·29	6·34	0·001	1·00	96·9	11·06	0·46	54·2
12	7·96	7·01	0·002	1·10	37·7	12·47	0·46	54·3
13	8·97	7·87	0·003	1·15	31·1	14·56	0·46	54·8
14	9·91	8·63	0·004	1·25	17·5	17·20	0·46	54·6
15	10·77	9·34	0·008	1·35	8·89	19·74	0·45	54·6

in the initial solution, the extraction of uranium does not follow the second-power dependence, as seen from the curve in Fig. 3. Neither of the previous uranyl chloride studies[2-10] deal with the extraction of uranium at these low acid concentrations. By plotting the mmoles of uranium versus mmoles of chloride extracted into TBP, the curve shown in Fig. 4 was obtained. The intersection of the two parts of the curve, which occurs at a chloride content of about 1·4 mmoles in the equilibrium organic phase, shows a chloride to uranium ratio of three. The first part of the curve has a slope very near to three. Both the slope and the point of intersection indicate that each uranium atom is extracted into the organic phase together with three chloride ions. When the uranium is almost completely extracted (0·46 mmole) into the TBP, free HCl begins to pass into the organic phase. This phenomenon probably accounts for the differences in the distribution of HCl in the absence and in the presence of uranium at low acid concentrations in the initial solutions, as already pointed out. This point will also be further discussed later.

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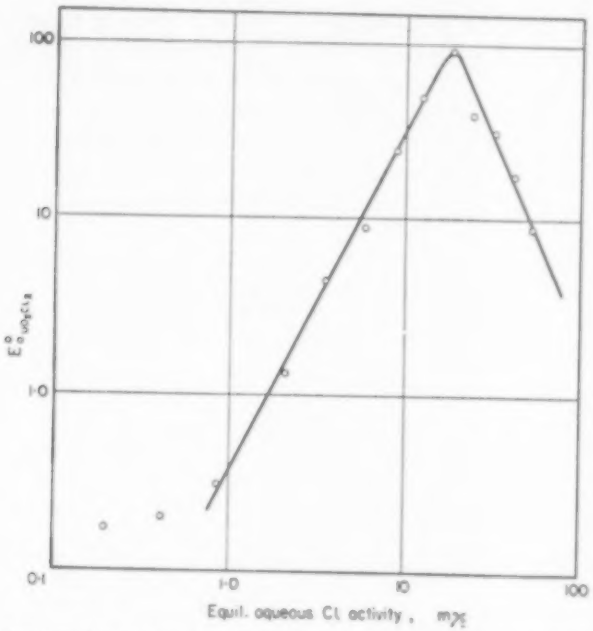

FIG. 3.—Log-log plot of the extraction ratio E_a^o of uranyl chloride against chloride activity in the equilibrium aqueous phase.

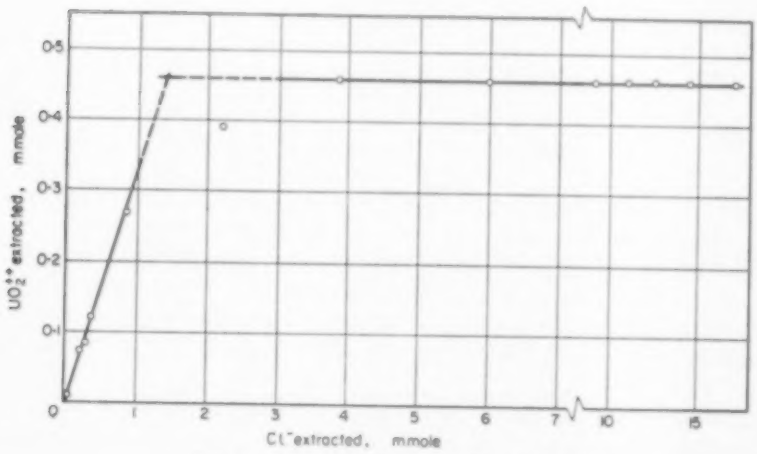

FIG. 4.—UO_2^{2+} and Cl^- extracted into 100% TBP.

Extraction of macro-quantities. The saturation effect

Our attempts to understand the competition between hydrochloric acid and uranyl chloride for the available extractant when they form extractable solvated molecules during their co-extraction from aqueous solution, have led us to carry out a study of the extraction of uranium from hydrochloric acid solutions, when both solutes are present in the initial aqueous solutions in comparable concentrations, sufficiently high

to approach "saturation" of the extractant. After a number of preliminary experiments, the final set was chosen at a constant acid concentration of 8·83 M. The uranium stock solution was 3·21 M UO_2Cl_2 at this acid concentration. The composition of the experiments is shown in Table 2, together with the distribution data.

Figs. 5–7 show the variation of the density, viscosity and conductivity respectively with the amount of uranium extracted. Table 2, column 5, shows the extent to which mutual miscibility of the layers is dependent upon the initial composition of the

TABLE 2.—THE DISTRIBUTION OF 8·83 M HCl AND UO_2Cl_2 BETWEEN WATER AND UNDILUTED TBP AS A FUNCTION OF THE URANIUM CONCENTRATION IN THE INITIAL SOLUTION. PHASE VOLUMES 5 ml (18·35 MMOLES TBP).

No. of Exp.	UO_2Cl_2 (M)		HCl, (M) Equil. aq. phase	Swelling of the organic phase, V, (ml)	$E^{\circ}_{a_{UO_2Cl_2}}$	Extracted into the organic phase, mmole		
	Init. aq. soln.	Equil. aq. phase				acid	uranium	water
1	2	3	4	5	6	7	8	9
100	—	—	7·57	1·15	—	15·01	—	55·2
101	0·32	0·002	7·43	0·90	189·0	12·15	1·60	48·5
102	0·64	0·009	7·89	0·80	58·8	10·09	3·17	37·6
103	0·96	0·036	8·29	0·75	22·6	8·42	4·66	30·4
104	1·28	0·12	8·36	0·65	8·99	7·12	5·91	23·1
105	1·60	0·30	8·40	0·55	4·07	6·30	6·70	18·9
106	1·93	0·57	8·44	0·50	2·26	5·74	7·07	16·8
107	2·25	0·84	8·43	0·40	1·62	5·11	7·37	15·6
108	2·57	1·14	8·53	0·40	1·23	4·63	7·59	14·9
109	2·89	1·46	8·57	0·40	0·98	4·43	7·74	15·2
110	3·21	1·77	8·65	0·40	0·83	4·12	7·87	13·6

aqueous phase or, more precisely, upon the amount of uranium extracted. The three figures, as well as the data on the volume swelling in column 5, show abundant evidence that the nature of the organic phase changes markedly when the uranium content reaches a TBP : uranium mole ratio of about three. The sharp increase in the density, viscosity and resistance values might indicate that a different chemical mechanism controls the extraction of uranium from the above TBP : U ratio and upwards.

The extraction ratio decreased as the total amount of uranium present was increased at constant acid concentration. If this effect is to be quantitatively studied the acid concentration must be carefully controlled, because the extraction is largely dependent on the acid concentration, and the total amount of uranium in the initial aqueous solution was kept sufficiently high to minimize the effect of the acid upon ionic strength. This is an additional reason why high concentrations of solutes were chosen. Fig. 8 is a graph of uranium versus acid content in mmole in the equilibrium organic phase; a break in the curve appears at a UO_2Cl_2:GCl ratio of about one. At this intersection the TBP:UO_2Cl_2 ratio approximates to three. The first part of the curve has a slope of unity, and the second part a slope of two. We would interpret

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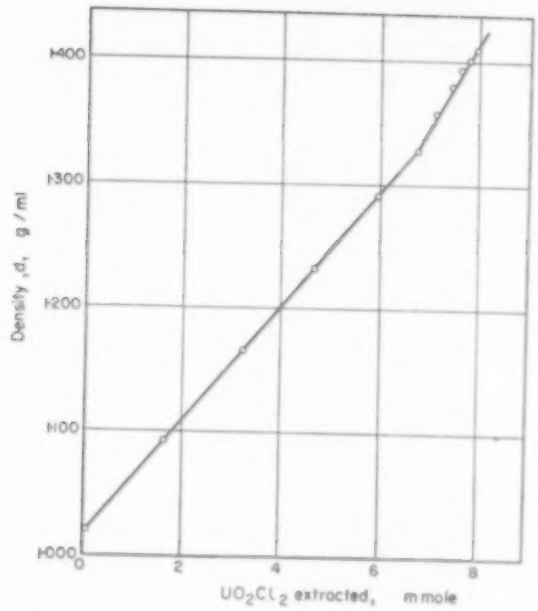

FIG. 5.—Density of the equilibrium organic phase as a function of UO_2Cl_2 content.

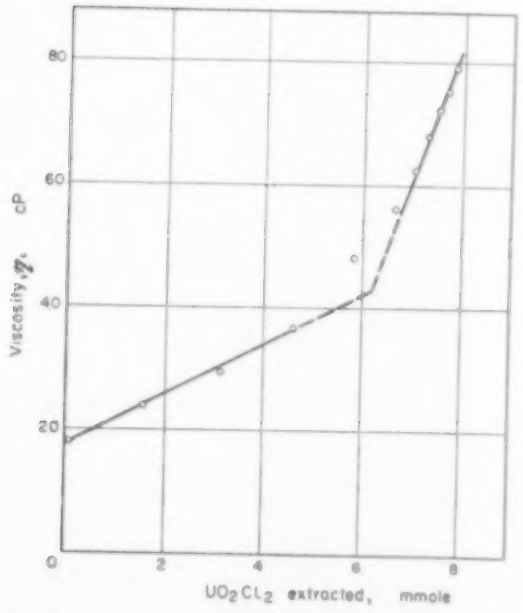

FIG. 6.—Viscosity of the equilibrium organic phase as a fucntion of UO_2Cl_2 content.

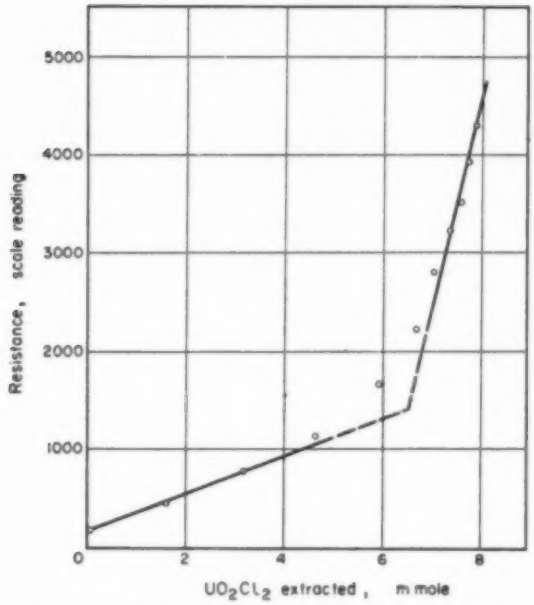

FIG. 7.—Resistance of the equilibrium organic phase as a function of UO_2Cl_2 content.

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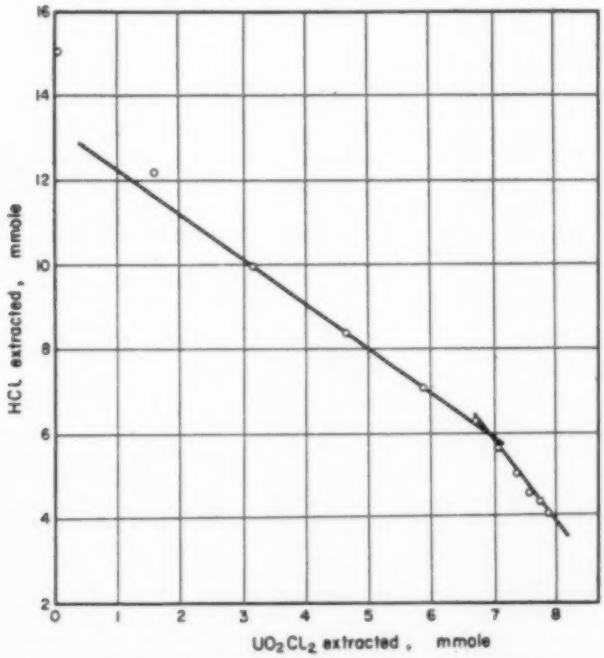

FIG. 8.—HCl and UO_2Cl_2 extracted into 100% TBP.

this as showing that in the concentration range corresponding to the first part of the curve each uranyl chloride molecule forces out one acid molecule, while in the second part each uranyl forces out double the amount of acid.

There is evidence[22,23] that the uranyl nitrate molecule is unhydrated in the tributyl phosphate phase. The extraction of macro-quantities of uranyl chloride entails the transport of appreciable quantities of water from the organic phase back to the aqueous phase. A similar phenomenon was recently observed by IRVING and

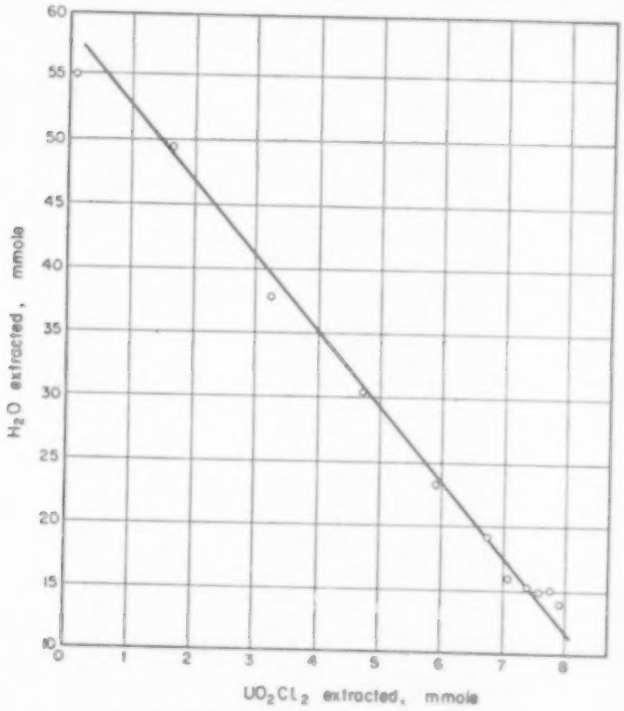

FIG. 9.—H_2O and UO_2Cl_2 extracted into 100% TBP.

EDGINGTON[2] during the extraction of macro-amounts of cobalt chloride into TBP. The amount of water in the organic phase is shown in Table 2, column 9, while Fig. 9 shows the graph of H_2O (mmole) versus UO_2Cl_2 (mmole) in the equilibrium organic phase. The line with a slope of six drawn through the points fits the values with a certain scatter in the lower part. Unfortunately, our Karl Fischer determinations are not accurate enough in this region; this is probably due to the high uranium content in the samples, which may interfere with the water determinations. If the slope of six is correct throughout the region, each uranyl chloride entering the organic phase forces out six molecules of water. This number six fits our scheme for the proposed extraction mechanism, as will be shown later.

Fig. 10 shows the spectrum of uranyl chloride in TBP. As the spectrum was fundamentally the same throughout the experiments 101–110, with varying UO_2Cl_2

[22] T. V. HEALY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 633 (1956).
[23] L. L. BURGER, *J. Phys. Chem.* **62**, 590 (1958).

and HCl content, it was possible to calculate the molar extinction for the wavelength range investigated. We estimate that our ε values are accurate within ± 8 per cent in the regions 400–415 mμ and 485–500 mμ and within ± 3 per cent in the region between 415 and 485 mμ. Because of this difference in accuracy, the possibility of different spectra in the two border regions cannot be excluded. The characteristic peaks of the spectrum at 420, 430, 445, 465 and 480 mμ are very close to those given by uranyl chloride in ethereal and ketonic solvents[24] in which category TBP may be included.[2]

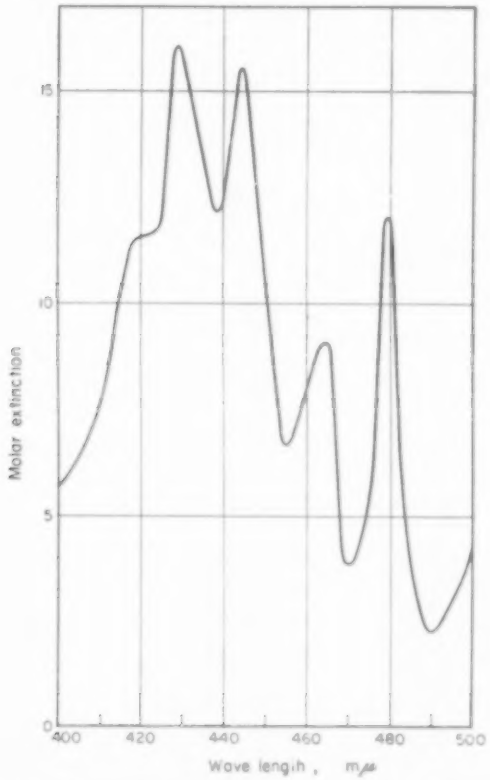

FIG. 10.—Absorption spectrum of uranyl chloride in undiluted TBP in presence of hydrochloric acid (see text.)

It must be pointed out, however, that HEALY and MCKAY[22] found no resemblance between uranyl nitrate spectra in these solvents. It is difficult to derive more conclusions from the spectrum because of lack of information from independent sources concerning the nature of the species in uranyl chloride solutions under various conditions.

The metal ion is not hydrolysed under the experimental conditions presented in this paper, and therefore the variation in the extraction ratio when the initial uranium concentration is increased tenfold must be attributed to polymerization of uranium in

[24] E. RABINOWITCH, ANL-5173 (1953).

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the aqueous phase[25–27], since it has been shown[27] that a decrease in percentage extraction with increasing initial metal ion concentration indicates polymerization of metal in the aqueous phase. In Fig. 11 log $[U]_a$ is plotted versus the logarithm of organic uranium molarity, log $[U]_o$. The slope of the first part of the curve is four, and of the second eight, indicating a greater degree of polymerization of uranium in the aqueous phase. The increasing change in the slope of the curve with increase in uranium concentration shows evidence of more than one polymer present. Following IRVING *et al.*[28] Fig 12 was constructed to show the extent of polymerization in organic and aqueous phases. The slope is negative, again indicating a higher degree of polymerization in the aqueous phase than in the organic phase.

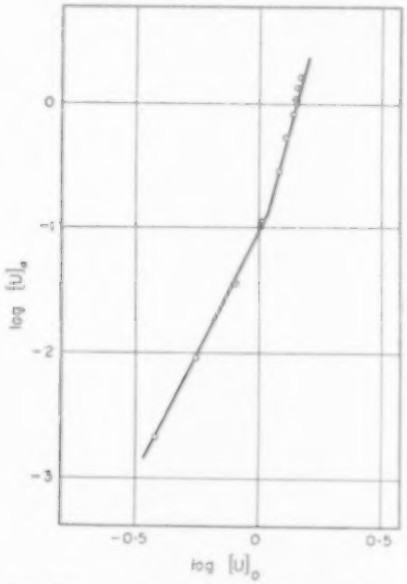

FIG. 11.—Log–log plot of the uranium(VI) content of the equilibrium aqueous phase against its content in the equilibrium organic phase.

DISCUSSION

The solubility of water in TBP indicates that a TBP-monohydrate is formed by hydrogen bonding.[12] This does not seem to undergo auto-ionization, probably owing to the double hydrogen bond involved,[15] as was shown from conductance and viscosity determinations. The affinity of TBP for water does not decrease as the uptake of hydrochloric acid by TBP increases, and it was suggested[12,14] that for low acid concentrations of up to about 1 M HCl in the initial aqueous solution the main interaction remains that of the binary system of TBP–H_2O rather than that of the ternary system containing in addition hydrochloric acid. Therefore, it should not be surprising that at low hydrochloric acid concentrations up to approximately 1 M the basic ternary system of H_2O–HCl–TBP is not completely identical with the

[25] A. E. LEVITT and H. FREUND, *J. Amer. Chem. Soc.* **78**, 1545 (1956).
[26] R. J. MYERS, D. E. METZLER and E. H. SWIFT, *J. Amer. Chem. Soc.* **72**, 3767 (1950).
[27] R. E. CONNICK and W. H. REAS, *J. Amer. Chem. Soc.* **73**, 1171 (1951).
[28] H. IRVING, F. J. C. ROSSOTTI and R. J. P. WILLIAMS, *J. Chem. Soc.* 1906 (1955).

four-component system H_2O–HCl–UO_2Cl_2–TBP and, furthermore, not surprising that the ligand dependency of the extracted uranium is different from that at higher acid concentrations. Comparing the amounts of HCl extracted from water[12] with those from aqueous uranium chloride solutions at identical initial acid concentrations, given in Table 1 and plotted in Fig. 4, one can see that the uranyl chloride plays the rôle of salting-out agent for the hydrochloric acid. This mutual salting-out effect is probably responsible for the HUO_2Cl_3, molecular or ion-paired, species

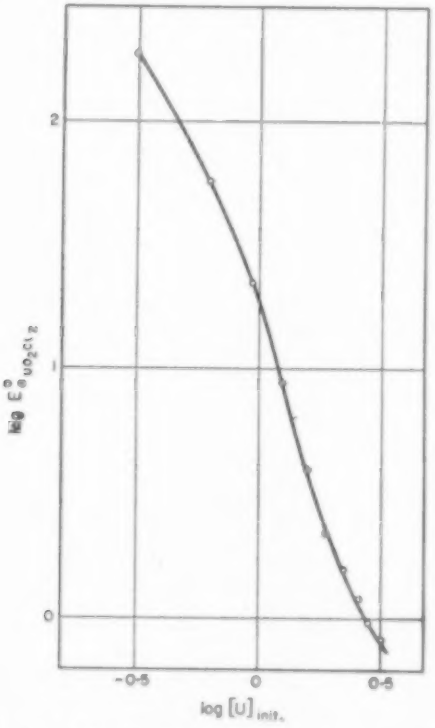

FIG. 12.—Log–log plot of the extraction ratio of uranium(VI) against its concentration in the initial aqueous solutions.

existing in, or extracted into, the TBP phase at low acid concentrations. This behaviour of the system for initial acid concentrations below 1 M is in marked contrast to that at higher acid concentrations. It seems quite safe to assume from our experiments, and also in accordance with those published by other authors[2,3,9], that for acid concentrations between 1 M and approximately 7 M HCl, the uranium species extracted has the simple composition UO_2Cl_2. The extraction ratio reaches a maximum at acid concentrations between 7 M and 8 M HCl, as shown in Fig. 3. This agrees with the results obtained by IRVING and EDGINGTON[2], ISHIMORI and NAKAMURA[4] and SHEVCHENKO *et al.*[9] For higher acid concentrations the extraction ratio decreases with increasing HCl concentration in the initial aqueous solution. This range of acid concentration appears to correspond to a maximum extraction ratio for a number of other bivalent metal chlorides.[2]

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The different solvation number of hydrochloric acid in TBP, as found from a previous investigation,[12] offers the most tempting explanation for the "maximum range" phenomenon recorded, since it is very unlikely that a simple competition exists between the solutes for the available TBP molecules, one of the solutes (in this case uranyl chloride) being a minor constituent of the system, and the other constituent (in our case HCl) being nearly one hundred times in excess. The possibility of several solvates appearing for the same inorganic species at various acid concentrations of the initial solution is known (see for example Ref. (29). There is an equilibrium between two different solvates and, in general, the higher solvate gives place to the lower in concentrated solution. This is the case in our basic ternary system H_2O–HCl–TBP. It was found that for concentrations of acid up to about 7 M HCl in the initial aqueous solution, the only species existing in the organic phase is the hydrochloric acid–disolvate–hexahydrate, $[HCl\cdot(TBP)_2\cdot(H_2O)_6]$. At this concentration all the TBP is bound in the complex. Further uptake of HCl by the organic phase results in a progressive degradation of the disolvate according to the equation

$$[HCl\cdot(TBP)_2\cdot(H_2O)_6]_{(o)} + HCl_{(a)} \rightarrow 2[HCl\cdot TBP\cdot(H_2O)_2]_{(o)} \quad (1)$$

and leads to increased formation of a hydrochloric acid–monosolvate trihydrate. The formation of the monosolvate begins when the initial acid concentration exceeds 7 M. This new compound, the monosolvate, is the only one competing with uranyl chloride for the available TBP: increase in its formation in the organic phase progressively forces the uranyl chloride out of the organic phase.

In order to check the above assumption, the second set of experiments was chosen. A concentration of 8·83 M HCl in the initial solution already causes the formation of a rather significant amount of the monosolvate in the opposing equilibrium organic phase. The high concentration of uranyl chloride, on the other hand, should enable us to prove quantitatively the above chemical mechanism.

The interpretation derived from Fig. 8 is compatible with the formation of a uranyl chloride–disolvate[3,9] and the replacement of the hydrochloric acid–disolvate could be represented as follows:

$$[HCl(TBP)_2\cdot(H_2O)_6]_{(o)} + UO_2Cl_{2(a)} \rightarrow [UO_2Cl_2\cdot(TBP)_2]_{(o)} + HCl_{(a)} + 6H_2O_{(a)} \quad (2)$$

where for each UO_2Cl_2 entering the organic phase, one molecule of HCl and six molecules of H_2O are forced out of it, as the slopes in Figs. 8 and 9 indicate. As long as the species $[HCl\cdot(TBP)_2\cdot(H_2O)_6]$ exists in the organic phase, no serious competition takes place between the acid and the uranium for the available TBP molecules. Only on further increase of the uranium concentration does real competition start between the solutes when passing into the organic phase. This competition could be represented by the equilibrium

$$2[HCl\cdot TBP\cdot(H_2O)_2]_{(o)} + UO_2Cl_{2(a)} \rightleftarrows [UO_2Cl_2\cdot(TBP)_2]_{(o)} + 2HCl_{(a)} + 6H_2O_{(a)} \quad (3)$$

as indicated by the slope of the second part of the curve in Fig. 8 and by the slope in Fig. 9.

When a certain concentration of uranium is reached in the equilibrium organic

[29] E. Hesford, H. A. C. McKay and D. Scargill, *J. Inorg. Nucl. Chem.* **4**, 321 (1957).

phase, all the acid–disolvate has been replaced by uranyl chloride and the organic phase contains excess of acid only as the monosolvate

$$[HCl\cdot(TBP)_2\cdot(H_2O)_6]_{(o)} + [HCl\cdot TBP\cdot(H_2O)_3]_{(o)} + UO_2Cl_{2(a)} \rightarrow$$
$$[UO_2Cl_2(TBP)_2]_{(o)} + [HCl\cdot TBP\cdot(H_2O)_3]_{(o)} + HCl_{(a)} + 6H_2O_{(a)} \quad (4)$$

At this point, markedly shown in Figs. 5–8, the organic phase contains uranium corresponding to a UO_2Cl_2 : TBP mole ratio of 1 : 3. Although it is true that this mole ratio approaches the value 1 : 2 asymptotically under the experimental conditions presented in this paper, the fact that the ratio 1 : 3 is exceeded only with difficulty shows that the compounds $[HCl\cdot TBP\cdot(H_2O)_3]$ and $[UO_2Cl_2\cdot(TBP)_2]$ are of comparable stability, and on their passing into the organic phase, side by side with the mutual salting-out from the aqueous phase, both components force each other from the organic solvent.

According to the chemical mechanism suggested above, it is neither the saturation effect, nor the higher polymerization of uranium in the aqueous phase which operates against the salting-out effect, but the competition between two complexes of comparable stability.

The amount of water accompanying HCl into the solvent has previously been determined. New measurements in this study have shown that if the concentration of uranium is not too low, about six molecules of water are forced out of the organic phase by each molecule of UO_2Cl_2 entering it. $UO_2Cl_2\cdot 2TBP$ seems therefore to be unhydrated, as is the corresponding nitrate solvate.[23] A progressive displacement of water by uranyl nitrate, as the concentration of the latter is increased, was reported by HEALY and MCKAY. This displacement finally results in a solution of anhydrous uranyl nitrate in TBP.[22]

According to the above explanation, $UO_2Cl_2\cdot 2TBP$ seems to be unhydrated, and apparently unable to take up a third chloride atom. Nevertheless, it is impossible to infer from the measurements carried out in this investigation whether a particular species identified in the organic phase has crossed the phase boundary as such, or has been formed by the interaction of two or even more species in the organic phase in equilibrium with the opposing aqueous phase. Furthermore, in practice there are never "ideal" heterogeneous equilibrium conditions, as defined by IRVING *et al.*[28], and therefore it is not certain whether UO_2Cl_2 does not react chemically with HCl in the TBP phase, in contrast to $UO_2(NO_3)_2$ and HNO_3 in TBP, where no such interaction was found to exist.[22] It is indeed not at all improbable that the additional acid molecule in the TBP phase reacts with the uranyl chloride–disolvate and that the true species has the composition $[HUO_2Cl_3\cdot 3TBP\cdot 3H_2O]$. In such a case a progressively lower solvate formation accounts for all the differences appearing in our experiments. The existence of this latter compound could also be explained if the additional acid molecule is associated with the co-ordinated solvate molecule and not directly attached to the uranium; thus, it might be represented as $[UO_2Cl_2\cdot 3TBP\cdot HCl\cdot 3H_2O]$.

Finally, we must point out that we can in no way claim that the properties of nearly saturated solutions discussed above are, as far as the determination of the salt solvation number is concerned, more exact than those derived from the conventional extractant–dilution experiments. The latter are carried out under more ideal thermodynamic conditions which were very different from those discussed in this paper.

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J. Inorg. Nucl. Chem., 1961, Vol. 16, pp. 323 to 336. Pergamon Press Ltd. Printed in Northern Ireland

A SUMMARY OF TTA EXTRACTION COEFFICIENTS*

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(*Received* 17 *May* 1960)

Abstract—Extraction with organic solutions of 2-thenoyltrifluoroacetone (TTA) has proved to be a versatile and powerful method for radiochemical separations. A summary of the data in the literature is presented. In general, the logarithm of the extraction coefficient is linear with pH at constant TTA concentration. The slope of this linear relationship and the pH of 50 per cent extraction for 0·2 M TTA in benzene are presented for forty-eight elements in the form of a periodic table. A graph is given by which one may quickly estimate per cent extraction as a function of pH. An equation for the variation of extraction with TTA concentration is given and the effect of changing the organic solvent is discussed.

New experimental data are presented for the extraction of Pa(V) and Fe(III) from hydrochloric acid.

THE chelating agent 2-thenoyltrifluoroacetone (usually abbreviated as TTA) has proved to be a valuable reagent for the solvent extraction of many metal ions. It was designed to provide extraction from stronger acid solutions than other chelating agents.[1]† Thus there is a wide range of metal ions that may be extracted without interference from hydrolysis. The high power dependence of the extraction on acidity makes the separation of one metal ion from another very sharp. Because of the widespread use of this technique, there are scattered data in the literature on extraction coefficients for many elements under various conditions. A survey of these data has been made in order to provide a compilation for the purpose of facilitating the design of new radiochemical separation procedures and the estimation of impurities not likely to be removed by existing procedures.

A considerable amount of work has been done on the use of TTA in the recovery of plutonium from irradiated reactor fuel elements. This work on "The Chelate Process" has been summarized by CRANDALL and HICKS[2]. However, there have been many other papers on the use of TTA for various radiochemical separations as well as several recent summaries of data. HYDE[3] has reviewed the valuable applications of TTA to the separations of the actinide elements. MOORE[4], and MORRISON and FREISER[5] have listed the optimum pH of extraction for many elements. DYRSSEN[6]

* Research performed under the auspices of the U.S. Atomic Energy Commission. Presented before the 136th National Meeting of the American Chemical Society, September 1959.

** Present address: Department of Chemistry, Columbia University, New York, New York.

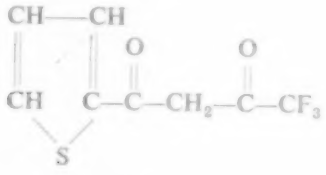
† The elements for which a reference contains extraction data are indicated in parentheses at the end of the reference. G stands for general reference.

[1] J. C. REID and M. CALVIN, *J. Amer. Chem. Soc.* **72**, 2948 (1950); CN-3343 (1945). [G]
[2] H. W. CRANDALL and T. E. HICKS, TID-2504 (1953). [U(IV), Nb(V), G]
[3] E. K. HYDE, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 281. United Nations, (1956). [G]
[4] F. L. MOORE, *Symposium on Solvent Extraction in the Analysis of Metals*. Special Technical Publication No. 238, A.S.T.M. (1958). [Fe(III), G]
[5] G. H. MORRISON and H. FREISER, *Solvent Extraction in Analytical Chemistry*. John Wiley, New York (1957). [G]
[6] D. DYRSSEN, *Svensk Kem. Tid.* **68**, 212 (1956). [G]

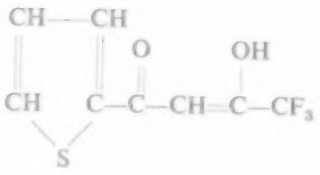
presented a table of extraction constants and recently SHEPERD and MEINKE[7] constructed a graph of per cent extraction versus pH for many elements. The present summary differs from the preceding ones in being more complete, in presenting the data taken under various experimental conditions on a uniform basis so that the relative extractabilities of the elements are more apparent, and in presenting the data in a form from which one may more readily estimate extraction as a function of pH, TTA concentration and solvent.

PROPERTIES OF TTA

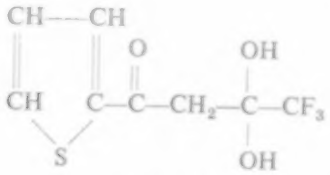
TTA is usually obtained as a light straw-yellow solid, molecular weight 222·2, m.p. 42·5–43·2°C. TTA may be purified by vacuum distillation. It is sensitive to light and should be stored in brown bottles. This chelating agent is a 1,3-diketone and exists in the following three forms:



Keto

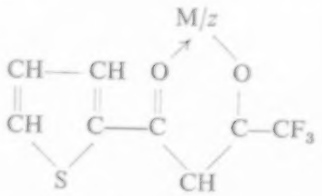


Enol



Keto hydrate

The TTA enolate ion forms highly extractable metal chelates of the form



where z is the charge on the uncomplexed metal ion. In the benzene phase TTA is about 11 per cent in the keto hydrate form, the rest in the enol form.[8] In dilute acid about 1·6 per cent of the TTA is in the enol form, the remainder in the keto hydrate form.[1] The stoicheiometric distribution coefficient (total TTA in benzene/total TTA in aqueous) is forty in dilute acid. The lowest value of the distribution coefficient is thirty-seven in 2 M $HClO_4$ and is sometimes much larger at high salt concentrations. Thus not more than $2\frac{1}{2}$ per cent of the TTA is in the aqueous phase at low pH values.

The stoicheiometric ionization constant of TTA has been studied by several

[7] E. SHEPERD and W. W. MEINKE, AECU-3879 (1958). [G]
[8] E. L. KING and W. H. REAS, *J. Amer. Chem. Soc.* 73, 1806 (1951); AECD-2573. [G]

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authors. The best value of pK_a at zero ionic strength and 25°C appears to be 6·38.[9] At high pH values, TTA is converted to the enolate ion, lowering its stoicheiometric distribution coefficient. The ratio of initial to final TTA concentration in benzene, when equilibrated with an equal volume of an aqueous phase, is given by

$$\frac{(TTA)_i}{(TTA)_o} = 1{\cdot}02 + 10^{-8}/[H^+]. \tag{1}$$

Thus at a pH of eight about half the TTA can be extracted into the aqueous phase. However if the pH of an aqueous solution of TTA is raised above nine, the TTA cleaves into trifluoroacetic acid and acetylthiophene faster than it enolizes.[9] Thus one must be careful when adjusting the pH of aqueous solutions of TTA with base not to exceed a pH of 9 even momentarily. However stable solutions of the enolate ion at higher pH may be prepared by dissolving anhydrous TTA in basic solutions.[9]

The stoicheiometric activity coefficient of TTA in benzene has been measured by KING and REAS[10]. They fit their data with the following equation:

$$f_{HT} = 1 - 0{\cdot}24(HT)_B^{0{\cdot}48} \tag{2}$$

where $(HT)_B$ is the concentration of TTA in benzene.

Besides solvent extraction, TTA has been used in colorimetry,[11] chromatography,[12] and ion exchange.[13] An interesting polarographic study of TTA has been made by ELVING and CALLAHAN[14].

THEORY

The equation for the extraction of a metal ion with charge $+z$, M^{z+}, can be simply written as

$$(M^{z+})_a + z(HT)_o = (MT_z)_o + z(H^+)_a$$

where subscripts a and o refer to the aqueous and organic phases respectively. A thermodynamic extraction constant for this process can be written as

$$K_{th} = \frac{Ef_{MT_z}(H^+)_a^z}{(HT)_o^z f_{HT}^z} \frac{\gamma_{H^+}^z}{\gamma_{M^{z+}}} \times \left[1 + k_1[X^-] + k_2[X^-]^2 + \ldots + k_{H1}/[H^+] + \ldots + k_{M1}\frac{[HY]}{[H^+]} + \ldots\right] \tag{3}$$

where E is the extraction coefficient (total concentration of metal in the organic phase/total concentration of metal in the aqueous phase), parentheses indicate concentration, f's organic phase activity coefficients, and γ's aqueous phase activity coefficients. The terms in the large square brackets correct for the fact that not all the metal in the aqueous phase is present as the bare uncomplexed, unhydrolysed metal ion. The individual terms indicate how one should correct for such processes as complexing

[9] E. H. COOK and R. W. TAFT, JR., *J. Amer. Chem. Soc.* **74**, 6103 (1952); NYO-3374. [G]
[10] E. L. KING and W. H. REAS, *J. Amer. Chem. Soc.* **73**, 1804 (1951); AECD-2573. [G]
[11] A. K. DE and S. M. KHOPKAR, *Chem. & Ind.* No. 26, 854 (1959). [G]
[12] E. W. BERG and R. T. MCINTYRE, *Analyt. Chem.* **26**, 813 (1954). [G]
[13] R. A. JAMES and W. P. BRYAN, *J. Amer. Chem. Soc.* **76**, 1982 (1954). [G]
[14] P. J. ELVING and C. M. CALLAHAN, *J. Amer. Chem. Soc.* **77**, 2077 (1955). [G]

with the anion X^-, hydrolysis, and complexing with the anion of the weak acid HY. The latter may even stand for the formation of aqueous metal–TTA complexes. So far it has been assumed that the only metal species in the organic phase is the uncharged chelate MT_z. This has been shown to be true many times by the dependence of Ef_{MT_z} on the z^{th} power of the TTA activity. There are a few exceptions to this rule which will be discussed below.

The quantity f_{MT_z} has been measured for U(IV) in benzene as a function of TTA concentration.[15] Within experimental error, it was found to be equal to f_{HT} at the same TTA concentration. It has often been assumed for other metals that $f_{MT_z} = f_{HT}$ independent of chelate concentration, and equation (3) simplified accordingly. We will in general adopt this procedure. There is an exception to this rule however for uranyl ion. Several workers[16,17,18] have found that f_{MT_z} for the uranyl ion is considerably less than f_{HT}. This has been interpreted[16,17] as resulting from the combination of the chelate, UO_2T_2, with an HT molecule to form the weak complex $UO_2T_2 \cdot HT$ with a formation constant of two. Thus f_{MT_z} for U(VI) is given by

$$\frac{f_{HT}}{1 + 2(HT)f_{HT}}. \tag{4}$$

Equation (3) has been used for many studies of complex and hydrolysis constants[19] and if one had values of the K_{th} in equation (3) for many elenents, it would provide interesting structural chemical information. (See reference 6.) However, from the radiochemist's point of view one needs only to conveniently reproduce the extraction data. It has been found that the following equation fits almost all the experimental data in dilute solution.

$$K = \frac{E[H^+]^x}{(HT)^z f_{HT}^{(z-1)}} \tag{5}$$

There is no theoretical reason why x is a constant when it is not equal to z. It does appear, however, that within experimental error log E is generally linear with pH at constant TTA concentration. The parameter x may differ from z because it includes the effects of $\gamma_{M^{z+}}$ and the terms in the brackets in equation (3). It was also found for strong acid solutions that if one used the acid concentration instead of $[H^+]$ in equation (5), that one also generally found a linear relationship within experimental error. Of course the parameter x now includes other effects but is still surprisingly constant.

If aqueous metal–TTA complexes were formed then the z as well as the x of equation (5) would appear to be smaller than the value of z which one would use in equation (3). However, for most cases that have been measured the apparent TTA power dependence is still z. Also, it will be shown in a later section that the directly measured aqueous TTA complexes are usually not strong enough to affect the apparent value of z in the region of interest by more than about two-tenths of a unit. Thus the value of z in equation (5) has usually been taken to be the charge of the bare ion in the aqueous phase. This is the oxidation state of the metal, except for oxygenated cations, such as U(VI) and Pu(VI), which have a charge of +2.

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SUMMARY OF EXTRACTION DATA

A critical review of the available data on TTA extractions using benzene as the organic solvent has been made using equation (5) when the experimenter measured the pH of his solutions. For experiments in strong acid where the acidity was determined by titration, the hydrogen ion concentration was substituted for $[H^+]$ in equation (5). For most of the data the metal ion concentration was small compared to the TTA concentration. When this was not the case, the free TTA concentration in the organic phase was calculated and used in equation (5). The values of the parameters K and x which best fit the data are presented in Table 1. Notice that it is necessary to use different values of K and x for different aqueous media, such as strong HCl or HNO_3. However, the values of K and x should be independent of the TTA concentration at which the measurements were made. To make it more convenient to use the numbers, the mid-point of the extraction curve for each element was calculated for a commonly used TTA concentration. Thus, pH_{50} was defined as the pH of 50 per cent extraction for an equal volume of 0·2 M TTA in benzene. It is related to K and x by the following equation:

$$pH_{50} = \frac{1}{x}(pK + 0{\cdot}75z - 0{\cdot}05). \tag{6}$$

The values of pH_{50} and x are presented in the form of a periodic table in Fig. 1 For the cases that have negative pH_{50}'s, the acid concentration has been used instead

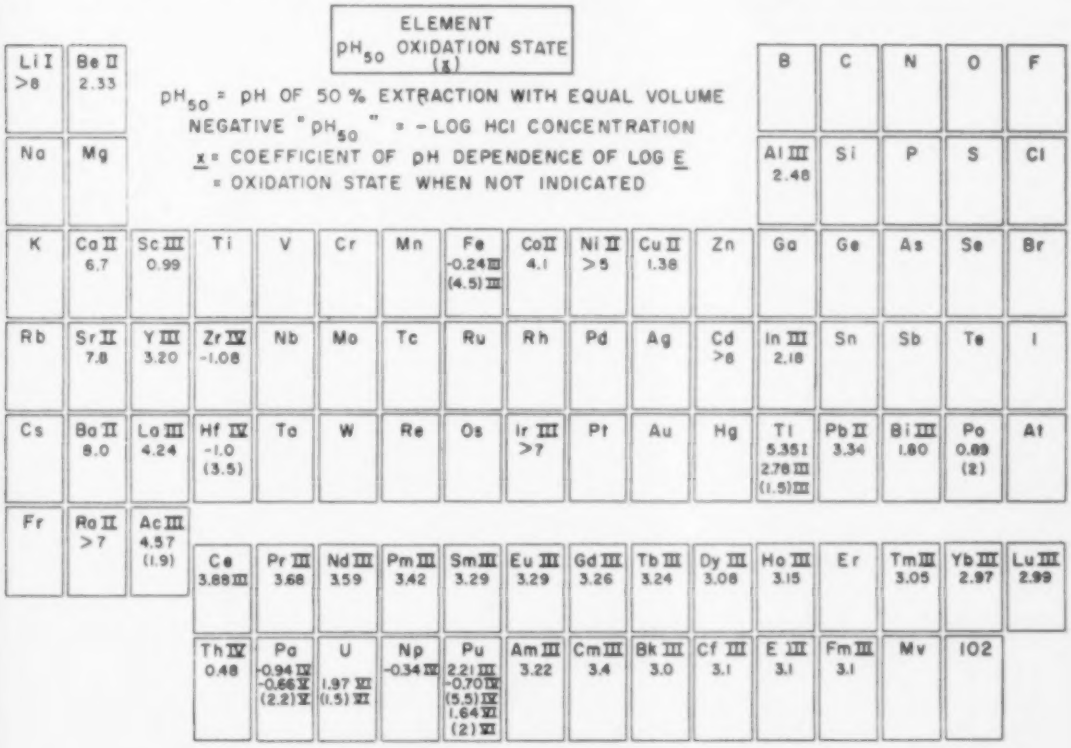

FIG. 1.—Extraction of the elements with 0·2 M TTA in benzene.

TABLE 1.—EXTRACTION PARAMETERS FOR BENZENE SOLUTIONS OF TTA

Element and oxidation state	Aqueous phase	x[a]	K[a]	pH_{50}[b]	Ref.	See also
Actinium (III)	Dil. NaCl	1·9	$3·3 \times 10^{-7}$	4·57	21	
Aluminum (III)	Low salt	3	$5·9 \times 10^{-6}$	2·48	22	
Americium (III)	Dil. acid	3	$3·5 \times 10^{-8}$	3·22	23	
Barium (II)		2	$\sim 2·3 \times 10^{-15}$	8·0[c]	24	
Berkelium (III)[d]	0·1 M $NH_4C_2H_3O_2Cl$	3	$\sim 1·5 \times 10^{-7}$	3·0	25	
Beryllium (II)[e]		2	$6·3 \times 10^{-4}$	2·33	22	
Bismuth (III)	Dil. NaCl	3	$6·2 \times 10^{-6}$	1·80	21	
Cadmium (II)				>8	26	
Calcium (II)	Dil. NaCl	2	1×10^{-13}	6·7[c]	27	
Californium (III)[d]	0·1 M $NH_4C_2H_3O_2Cl$	3	8×10^{-9}	3·1	25	
Cerium (III)	HCl + KCl, $\mu = 0·1$	3	$3·7 \times 10^{-10}$	3·88	28	30
	NaAc–HAc buffer	2·1	$3·0 \times 10^{-6}$	3·68	28	
	$(NH_4)_2SO_4$, $\mu = 0·1$	3	$4·0 \times 10^{-11}$	4·20	29	
Cobalt (II)		2	$\sim 2 \times 10^{-7}$	4·1	30	
Copper (II)	Low in salts	2	$4·8 \times 10^{-3}$	1·38	22	
Curium (III)[d]	0·1 M $NH_4C_2H_3O_2Cl$	3	1×10^{-6}	3·4	25	
Dysprosium (III)	HCl + KCl, $\mu = 0·1$	3	$9·3 \times 10^{-9}$	3·08	28	31
Einsteinium (III)[d]	0·1 M $NH_4C_2H_3O_2Cl$	3	6×10^{-9}	3·1	25	
Europium (III)	HCl + KCl, $\mu = 0·1$	3	$2·2 \times 10^{-8}$	3·29	28	
Fermium (III)[d]	0·1 M $NH_4C_2H_3O_2Cl$	3[f]	8×10^{-9}	3·1	25	
Gadolinium (III)	HCl + KCl, $\mu = 0·1$	3	$2·7 \times 10^{-8}$	3·26	28	
Hafnium (IV)[g]	HCl	3·5[h]	5×10^{5}	−1·0	32	
	2 M and 4 M $HClO_4$	3	$3·7 \times 10^{7}$	−1·54	33, 34, 35	46
	HNO_3 or HNO_3 + $NaNO_3$	3[h]	2×10^{8}	−1·4	36	46, 47
Holmium (III)	HCl + KCl, $\mu = 0·1$	3	$5·6 \times 10^{-8}$	3·15	28	
Indium (III)	Potassium acid phthalate + HCl	3	$4·6 \times 10^{-5}$	2·18	37	
Iridium (III)				>7	38	
Iron (III)	HCl[g]	4·5	$2·0 \times 10^{9}$	−0·24	This work	48, 24
	HNO_3	variable		~0·5	39	49
Lanthanum (III)	HCl + KCl, $\mu = 0·1$	3	$3·1 \times 10^{-11}$	4·24	28	50
	NaAc–HAc buffer	2·1	$5·2 \times 10^{-7}$	4·04	28	
	Dil. acid	3	$1·7 \times 10^{-10}$	3·99	23	24
Lead (II)	Dil. NaCl	2	$5·8 \times 10^{-6}$	3·34	21	
Lithium (I)	0·1 M LiCl			>8	This work	
Lutecium (III)	HCl + KCl, $\mu = 0·1$	3	$1·7 \times 10^{-7}$	2·99	28	
Neodymium (III)	HCl + KCl, $\mu = 0·1$	3	$2·7 \times 10^{-9}$	3·59	28	23
Neptunium (IV)[g]	HCl	4[h]	$3·6 \times 10^{9}$	−0·34	40	
	$HClO_4$ + $NaClO_4$, $\mu = 2$	4	$3·8 \times 10^{5}$	−0·66	41	
Nickel (II)	HNO_3			>5	42	
Plutonium (III)[g]	0·005 M $Fe(ClO_4)_3$, $\mu = 0·1$ ($LiNO_3$)	3	$3·6 \times 10^{-5}$	2·21	43	49
Plutonium (IV)[g]	HCl	5·5	$6·7 \times 10^{6}$	−0·70	44	
	1 M $HClO_4$	4	$7·0 \times 10^{6}$	−0·97	15	
	HNO_3	4	$2·2 \times 10^{6}$	−0·85	45	51, 52, 49
Plutonium (VI)[g]	0·05 M HNO_3	2[i]	$1·5 \times 10^{-2}$	1·64	43	
Polonium	Dil. NaCl	2	$4·6 \times 10^{-1}$	0·89	21	
Praseodymium (III)	HCl + KCl, $\mu = 0·1$	3	$1·4 \times 10^{-9}$	3·68	28	61
Promethium (III)	HCl + KCl, $\mu = 0·1$	3	$8·8 \times 10^{-9}$	3·42	28	
Protactinium (IV)[g]	6 N HCl with Cr^{2+}	4[f]	$5·2 \times 10^{6}$	−0·94	53	
Protactinium (V)[g]	HCl	2·2		−0·73[j]	This work	86
				−0·59[k]	This work	
Radium (II)	Dil. NaCl	2[f]		>7	21	
Samarium (III)	HCl + KCl, $\mu = 0·1$	3	$2·1 \times 10^{-8}$	3·29	28	
Scandium (III)	HCl + KCl, $\mu = 0·1$	3	$1·7 \times 10^{-1}$	0·99	28	27
Strontium (II)	Low in salts	2	$\sim 7·5 \times 10^{-15}$	7·8[c]	22, 54	
Terbium (III)	HCl + KCl, $\mu = 0·1$	3	$3·1 \times 10^{-8}$	3·24	28	
Thallium (I)	Dil. NaCl	1	$2·2_5 \times 10^{-5}$	5·35	21	

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TABLE 1—*continued*

Element and oxidation state	Aqueous phase	x[a]	K[a]	pH_{50}[b]	Ref.	See also
Thallium (III)	Dil. NaCl	1·5	$1·1 \times 10^{-2}$	2·78	21	
Thorium (IV)	Dil. NaCl	4	10	0·48	21	62, 59
	HNO_3[c]	4	7·9	0·51	55	62, 63
	0·1 M $HClO_4$ + $LiClO_4$, $\mu = 3$[d]	4[f]	7·5	0·52	56	64
Thulium (III)	HCl + KCl, $\mu = 0·1$	3	$1·1 \times 10^{-7}$	3·05	28	
Uranium (IV)[g]	$HClO_4$ + $NaClO_4$, $\mu = 2$	4	$1·9 \times 10^{5}$	−0·58	57	
	HNO_3	4	$1·5 \times 10^{6}$	−0·31	58	49
Uranium (VI)[h]	Dil. HNO_3	1·5[i]	$2·3_0 \times 10^{-2}$	1·97	59	18, 49
	$HClO_4$ + $LiClO_4$, $\mu = 2$[d]	2[i]	$5·5 \times 10^{-3}$	1·79	16	65, 17
Ytterbium (III)	HCl + KCl, $\mu = 0·1$	3	$1·9 \times 10^{-7}$	2·97	28	
Yttrium (III)	HCl + KCl, $\mu = 0·1$	3	$4·1 \times 10^{-9}$	3·20	28	24
Zirconium (IV)[g]	HCl	4	$1·8 \times 10^{7}$	−1·08	30	47
	HNO_3, $\mu \sim 2$	3	$1·3 \times 10^{6}$	−1·72	46	49
	2 M and 4 M $HClO_4$	3	$8·5 \times 10^{6}$	−1·99	33, 34 35, 19 60	

[a] K and x are the parameters in equation (5). z is equal to the oxidation state unless otherwise noted.
[b] pH of 50 per cent extraction into an equal volume of 0·2 M TTA in benzene. All data refer to room temperature or 25°C unless otherwise noted.
[c] See equation (1) for the initial TTA concentration necessary to give the equilibrium TTA concentration of 0·2 M.
[d] Calculated from toluene data by use of Table 2.
[e] This value applies only when the metal is extracted from the aqueous into the organic phase.
[f] This value of x has been assumed since no value was given in the original reference.
[g] Hydrogen ion concentration was used instead of activity.
[h] $z = 3$.
[i] $z = 2$.
[j] 20°C.
[k] 30°C.
[l] See equation (4).

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[45] D. L. HEISIG and T. E. HICKS, UCRL-1169 (1952). [Pu(IV), G]

References continued at foot of next page

of $[H^+]$, and only the parameters for hydrochloric acid media are presented in the figure. There are several elements which extract well but for which there is no information listed in Fig. 1. SMITH and MOORE[20] found that Ce(IV) extracts to the extent of 50 per cent from 3 N H_2SO_4 into 0·5 M TTA in xylene. CRANDALL and HICKS[2] list U(IV) as extracting as well from HCl as from HNO_3 and Nb(V) as extracting better than Sc.

To calculate the extraction coefficient at any pH or TTA concentration, one uses the following equation:

$$\log E = x(\mathrm{pH} - \mathrm{pH}_{50}) + z \log \frac{(\mathrm{HT})}{0{\cdot}2} + (z-1) \log \frac{f_{\mathrm{HT}}}{0{\cdot}89} \tag{7}$$

where f_{HT} is given by equation (2). For a 0·2 M TTA in benzene solution,

$$\log E = x(\mathrm{pH} - \mathrm{pH}_{50}). \tag{8}$$

Of course, the percent extraction is simply given by

$$\%E = \frac{100E}{E + V_a/V_o} \tag{9}$$

where V_a and V_o are the volumes of the aqueous and organic phases respectively. To make it easier to use Fig. 1, Equations (8) and (9) have been combined and plotted in Fig. 2. Thus for integral values of x one can read off directly $\%E$ as a function of $\mathrm{pH}-\mathrm{pH}_{50}$. For TTA concentrations other than 0·2 M, one may substitute

$$\mathrm{pH}_{50}' = \mathrm{pH}_{50} - \frac{z}{x} \log \frac{(\mathrm{HT})}{0{\cdot}2} - \frac{z-1}{x} \log \frac{f_{\mathrm{HT}}}{0{\cdot}89} \tag{10}$$

for pH_{50} in the abscissa of Fig. 2.

OTHER SOLVENTS

Although benzene has been the most widely used solvent, there are some extraction data with other organic solvents. These are summarized in Table 2 as the difference between pH_{50}' (pH_{50} for the other solvent) and pH_{50} for benzene for a similar aqueous medium. For an estimate of the extraction with one of these solvents, one may

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TABLE 2.—EFFECT OF OTHER SOLVENTS

Solvent	$pH_{50}'-pH_{50}$[a]	Elements	Reference
Toluene	0·2	Am, Eu, Yb	25
Xylene[b]	0·0	Np(IV)	66
Xylene[b]	0·2	Th	67
Xylene[b]	0·4	Pu(IV)	68
Xylene[b]	1·3	Zr	69
s-butyl benzene	0·1	Pu(IV)	45
Monochlorobenzene	0·1	Pu(IV)	51
o-dichlorobenzene	0·3	Hf, Zr	34
o-dichlorobenzene	0·1	Pu(IV)	51
Trichlorobenzene	0·2	Pu(IV)	51
Chloroform	0·4	Pu(IV)	51
Bromoform	0·3	Pu(IV)	51
Carbon tetrachloride	0·0	Pu(IV)	51, 52
Carbon tetrachloride	0·1	Th	70
Tetrachloroethylene	0·1	Pu(IV)	51
Methyl isobutyl ketone	0·6	Zr	71
Methyl isobutyl ketone	0·3	Pu(IV)	71
Methyl isobutyl ketone	0·1	Th	70
Methyl isobutyl ketone	−0·7	U(VI)	71

[a] pH_{50} with indicated solvent minus pH_{50} with benzene.
[b] 0·5 M TTA.

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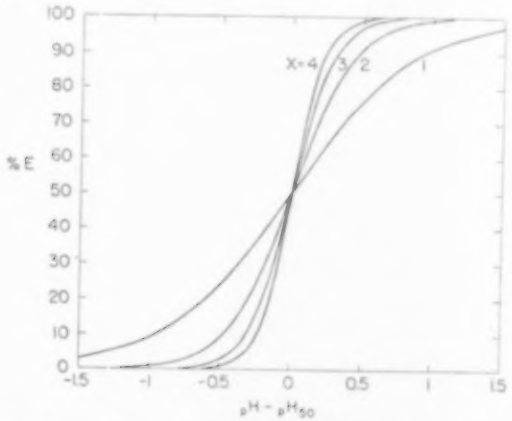

FIG. 2.—Per cent extraction vs. $pH-pH_{50}$ for integral values of the parameter x.

substitute pH_{50}' for pH_{50} in the abscissa of Fig. 2. For elements not listed in Table 2 with the solvent of interest this procedure must be used with caution because of the variation of the solvent effect from element to element as shown in the data for xylene and methyl isobutyl ketone.

Although TTA extracts about as well in carbon tetrachloride as in benzene, it is

not quite as effective in most of the other solvents. An important exception is the extraction of U(VI) by TTA in methyl isobutyl ketone, where the solubility of the uranyl chelate is fifty times greater than in benzene.[71] It seems to be a general rule that oxygenated solvents markedly enhance the extraction of oxygenated cations.[72] As further examples, it seems that some of the elements of the first transition series

TABLE 3.—FORMATION CONSTANTS FOR AQUEOUS TTA COMPLEXES

Element	log K_1[a]	Medium	Reference
Al(III)	−0·70	0·1 M HNO_3	78
Cu(II)	−0·61	0·02 M HNO_3	78
Fe(III)	0·68	0·1 M $HClO_4$	79, 80
	0·40	0·1–0·2 M HNO_3	78
La(III)	−2·60	1 M $NaClO_4$	81
Li(I)	−5·94	dil. acid	81
Mg(II)	−4·01	2·25 M HNO_3	78
Pu(IV)	2·78	$\mu = 0$	80
	1·8	$\mu = 0·2$	80
	1·90	0·5 M HNO_3	79
Sc(III)	0·00	0·02 M HNO_3	78
Th(IV)	1·9	$\mu = 0$	80
	1·2	$\mu = 0·1$	80
	1·18	0·5 M $HClO_4$	79
	0·81	$\mu = 2$	64, 56
U(IV)	1·0	$\mu = 0·1$	80
	1·23	0·5 M HCl	79
U(VI)	−0·24	$\mu = 0$	18
	−0·82	dil. acid	16
Zn(II)	−3·28	2·25 M HNO_3	78
Zr(IV)	3·03	4 M $HClO_4$	60

[a] See equation (11). For U(VI), M^{z+} stands for UO_2^{2+}. All data at 25°C.

extract better with methyl isobutyl ketone as a solvent,[73] and it has been reported that it is a better solvent than benzene for extracting gross fission products with TTA.[74] Data have been obtained also for the extraction of La[75] and Al[76] with methyl isobutyl ketone as a solvent.

Activity coefficients of TTA in solvents other than benzene are poorly known. For carbon tetrachloride CUNINGHAME and MILES[52] give the quantity $f_{HT}/f_{PuT_4}^{\frac{1}{4}}$, which should approximate $f_{HT}^{\frac{1}{4}}$. For pentaether f_{HT} is given by CRANDALL and HEISIG[77].

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[73] G. HIGGINS and G. IDDINGS Univ. of Calif. (Livermore). Private communication (1959). [G]
[74] T. KIBA and S. MIZUKAMI, *Bull. Chem. Soc. Japan* **31**, 1007 (1958). [G]
[75] O. MENIS, T. C. RAINS and J. A. DEAN, *Analyt. Chem.* **31**, 187 (1959). [La]
[76] H. C. ESHELMAN, J. A. DEAN, O. MENIS and J. C. RAINS, *Analyt. Chem.* **31**, 183 (1959). [Al]
[77] H. W. CRANDALL and D. L. HEISIG, UCRL-778 (1950). [G]
[78] R. W. TAFT JR. and E. H. COOK, *J. Amer. Chem. Soc.* **81**, 46 (1959); NYO-6587. [G]
[79] E. L. ZEBROSKI, BC-63 (1947). [G]
[80] A. E. MARTELL and M. CALVIN, *Chemistry of the Metal Chelate Compounds*. Prentice-Hall, New York (1952). [G]
[81] K. L. MATTERN, UCRL-1407 (1951). [G]

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AQUEOUS-PHASE COMPLEX FORMATION

Several workers have studied the formation of the first metal–TTA complex in aqueous solution. The values of the concentration formation constants

$$K_1 = \frac{(MT^{(z-1)+})(H^+)}{(M^{z+})(HT)} \tag{11}$$

are given in Table 3. By matching these first aqueous complex constants with the appropriate overall extraction constants (K) from Table 1 it is possible to show that a rough relationship of the following form exists:

$$(1/z) \log K = (1{\cdot}1 \pm 0{\cdot}1) \log K_1 - (0{\cdot}6 \pm 0{\cdot}3).$$

This is the evidence for the statement made earlier that the aqueous TTA complexes do not seriously affect the apparent value of z in the region about pH_{50}. However,

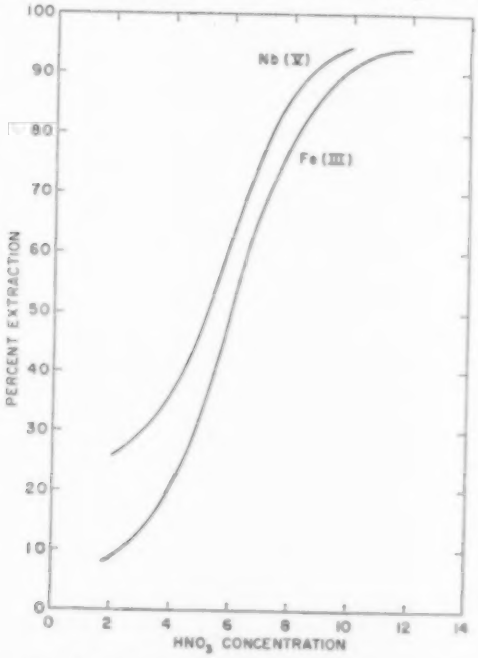

FIG. 3.—Extraction of Fe(III) and carrier-free Nb(V) from concentrated nitric acid. See references (4) and (82).

it should be noted that if one were to extrapolate to very large values of the extraction coefficient at high TTA concentration and high pH, then the values of both z and x would be reduced somewhat because of formation of aqueous TTA complexes.

ANOMALIES

An important anomaly is the work of MOORE on the extraction of Fe(III)[4,82] and carrier-free Nb(V)[82] from strong nitric acid solutions with an equal volume of 0·5 M TTA in xylene. The extraction curves, which are shown in Fig. 3, indicate an

[82] F. L. MOORE, W. D. FAIRMAN, J. G. GANCHOFF and J. G. SURAK, *Analyt. Chem.* **31**, 1148 (1959). [Fe(III), Nb]

increase in extraction with increase in acidity. This interesting and useful phenomenon is not explained and would seem to warrant further investigation.

Vanadium (IV) has an unusual extraction curve which passes through a maximum at a pH of about four for 0·25 M TTA in benzene.[83]

There are some cases where the apparent value of z appears less than what one would predict from the oxidation state of the ion. If one is using an oxygenated organic solvent in which one expects to find some metal salt extraction even in the absence of TTA, then, of course, the average number of TTA molecules per metal atom in the organic phase will be less than the valence of the metal ion.[72] It has been shown that *s*-butylbenzene extracts mixed TTA–nitrate metal complexes.[45] Even for benzene it has been claimed that at high chloride concentrations for Zr and Hf some mixed TTA–chloride complexes are extracted.[32,47] SCHERFF and HERRMAN[84] have presented some unusual data for the extraction of Zr from strong HCl with TTA with both benzene and xylene as solvents. Their extraction curves exhibit minima and in some cases show better extraction at a lower TTA concentration than at a higher concentration.

In general, temperature coefficients of TTA extractions are not as large as that measured for Pa(V) below.

The extraction of Fe(III) from dilute acid solutions is unusually slow (see references 24, 39 and below). However, the data of Fig. 3 were obtained under conditions where the equilibration time was only 5 min[4,82] and in reference (48) sufficient extraction was obtained in 10 min.

Beryllium is unusual in that its extraction is not only slow but also apparently irreversible.[22]

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EXPERIMENTAL TECHNIQUES

TTA extractions are generally considered slower than other types of solvent extractions. Many authors state that a half-hour of mechanical shaking or stirring is required to ensure equilibrium when extracting metals into the organic phase and that the back-extraction generally requires only a few minutes of mixing. However, the rate of approach to equilibrium depends on the degree of contact between the phases. Wrist-action hand shaking is usually faster than mechanical shaking. When only a few millilitres of solution are involved, a useful method is repeated rapid withdrawal of the two phases from a centrifuge cone into a transfer pipette followed by re-injection with a rhythm so as to produce an emulsion. Pre-equilibrating the TTA solution with dilute acid may speed up the extraction in some cases.

When the TTA extraction is the final step in the preparation of a carrier-free sample for counting, less solid material is obtained on the sample plate after ignition if the organic phase is evaporated directly* than if the activity is first back-extracted into an aqueous solution. This is important when α-particle emitters are to be counted. By a combination of this technique with that described in the preceding paragraph for small volumes of solution, nuclides with half-lives as short as one minute have been determined.[85]

NEW EXPERIMENTAL DATA

In order to provide data on the extraction of additional elements, extraction coefficients were measured for protactinium (V) and iron (III) from hydrochloric acid

* When organic solutions with low surface tension are evaporated, it is advantageous to use an apparatus which keeps the edge of the sample plate hotter than the centre.

[83] R. FUKAI and W. W. MEINKE, Progress Report No. 7, Dept. of Chem., Univ. of Mich., p. 63 (1958). [V(IV)]
[84] H. L. SCHERFF and G. HERRMAN, *J. Inorg. Nucl. Chem.* **11**, 247 (1959). [Zr]
[85] B. D. PATE, Washington University, St. Louis. Private communication (1959). [G]
[86] F. L. MOORE, *Analyt. Chem.* **27**, 70 (1955). [Pa(V)]

solutions. In addition, some qualitative data were obtained for magnesium and lithium.

TTA obtained from Peninsular Chem Research, Inc. was placed for a few hours in a vacuum desiccator. Besides drying the material, this treatment caused the TTA to appear less yellow, and reduced its odour considerably. This TTA was used without further purification to prepare a 0·200 M solution in thiophene-free benzene.

Protactinium-233 tracer was produced by the thermal neutron irradiation of $Th(NO_3)_4$. After the ^{233}Th produced had decayed to ^{233}Pa, the irradiated material

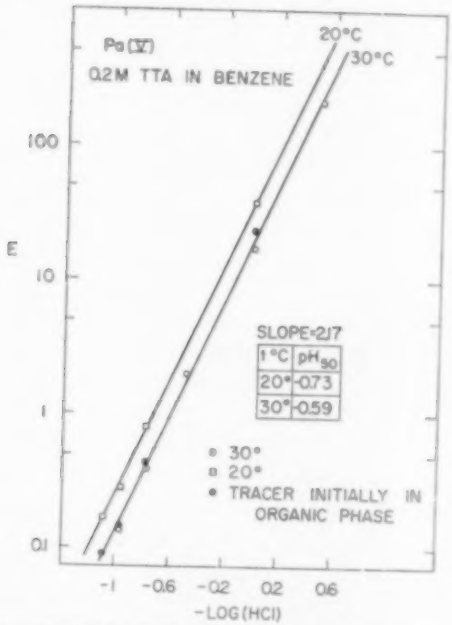

FIG.* 4.—The extraction of Pa(V) as a function of hydrochloric acid concentration.

was dissolved in 6 M HCl and the protactinium was purified by extraction into diisopropyl ketone and back-extraction into 1 M HCl. The resulting solution was washed with benzene to remove traces of diisopropyl ketone, evaporated almost to dryness in a polyethylene centrifuge cone, and diluted with 12 M HCl. The ^{59}Fe tracer was obtained from the Oak Ridge National Laboratory.

Ten millilitres of each phase was equilibrated in a long, thin glass-stoppered tube. The γ-ray activity of the two phases was determined as a function of time of equilibration without sampling by placing the tubes in a hole through a 3 in. NaI(Tl) scintillation counter.* The extraction coefficients for protactinium were found to depend strongly on temperature. For this reason, the equilibrations were carried out in constant temperature baths at 20° and 30°C. In some experiments, the activity was placed initially in the organic phase. The results of the protactinium experiments are shown in Fig. 4. The data at 9 M and 12 M HCl had to be corrected for the extraction of protactinium chloride into benzene. The data for this correction were

* This apparatus was designed by Dr. R. W. DODSON of this laboratory.

obtained by performing some equilibrations in which the organic phase was pure benzene. The results are shown in Table 4.

The extraction of iron (III) was found to be rather slow, requiring around 12 hr of shaking at room temperature to reach equilibrium. It was found necessary to

Table 4.—Effect of the extraction of Pa(V) into benzene

		30°		20°	
		E	*E* corr.	*E*	*E* corr.
9 N HCl	0·2 N TTA	0·169	0·136	0·319	0·278
		0·178*	0·145		
	No TTA	0·033	—	0·041†	—
12 N HCl	0·2 N TTA	0·198	0·04	0·369	0·17
		0·247*	0·09		
	No TTA	0·16	—	0·20	—

* Tracer initially in organic phase.
† Estimated.

make the aqueous phases 0·001 to 0·01 M in sodium dichromate to prevent the reduction of iron (III) to iron (II). The results are given in Table 1.

It was not possible to measure any extraction coefficients for magnesium with the tracer‡ used because of precipitation of the magnesium chelate. The solubility of this compound in benzene is apparently less than 10^{-4} M. This is surprising in view of the appreciable solubility of the calcium chelate.[27] No extraction was found for lithium at a pH of 7·5.

‡ ^{28}Mg obtained from the Hot Laboratory of the Brookhaven National Laboratory.

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J. Inorg. Nucl. Chem., 1961, Vol. 16, pp. 337 to 344. Pergamon Press Ltd. Printed in Northern Ireland

DINONYL NAPHTHALENE SULPHONIC ACID AND TRI-n-OCTYLAMINE AS LIQUID ION-EXCHANGERS FOR THE STUDY OF Fe(III) AND In(III)–CHLORIDE COMPLEXES*

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(*Received* 13 *June* 1960; *in revised form* 28 *June* 1960)

Abstract—The stability constant of the 1:1 Fe(III)–chloride complex at ionic strengths varying from 0·20 to 1·00 is independent of whether H^+ or Na^+ is the cation of the perchlorate ion. The specific ion effect on the stability of the $FeCl^{2+}$ complex found by COLL *et al.*, above 5 M, therefore is absent at these lower ionic strengths. For In(III), substitution of Na^+ for H^+ as cation of the perchlorate ion decreases the log K_1 of $InCl^{2+}$ by about 0·3 at ionic strengths of one and two. The presence of the specific ion effect on the In–Cl system at ionic strengths one and two and the absence of the effect on Fe–Cl system is not surprising since In(III) forms much more stable complexes with Cl^- than Fe(III). No extraction of the Fe(III) and In(III) by the anionic exchanger, tri-n-octylamine hydrochloride, in perchloric acid solutions, less than 2 M, has occurred. This indicates that perchlorate ion does not form negatively charged complex with Fe(III) or In(III) in the organic phase. The distribution coefficients of Fe(III) and In(III) are directly second power dependent upon the tri-n-octylamine hydrochloride concentration in the benzene phase, suggesting that the negatively-charged complexes $FeCl_5^{2-}$ and $InCl_6^{3-}$ complexes are formed in the organic phase.

COLL *et al.*[1] using a spectrophotometric method, determined the stability constant of the 1 : 1 Fe(III)-chloride complex in perchloric acid solutions. They found that the substitution of sodium perchlorate for part of the perchloric acid at a given total perchlorate concentration, above 5 M, decreases the complex stability constant. This constitutes the specific ion effect on the stability of the $FeCl^{2+}$ complex. It was of interest to determine whether specific ion effect was operative at lower ionic strengths for Fe(III)–chloride complex, and whether there is a specific ion effect on the stability of the In(III)–chloride complex.

Dinonyl naphthalene sulphonic acid, HD, and tri-n-octylamine, TOA, have been shown by BOYD and LINDENBAUM[2], to be strongly acidic and weakly basic anionic exchangers, respectively, and are analogs of resinous type exchangers. These liquid ion-exchangers offer several advantages over resinous ion-exchangers : they can be used for studies of equilibria in concentrated electrolyte solutions without Donnan penetration of the exchanger phase, the measurements of physical properties and analysis of the exchanger are more rapidly and conveniently performed than with the resinous exchangers. In this investigation dinonyl naphthalene sulphonic acid was used to obtain the stability constants of the 1 : 1 Fe(III) and In(III)–chloride complexes and the tri-n-octylamine was used to detect the nature of the negatively-charged complexes of Fe(III) and In(III).

* This investigation was supported by the U.S. Atomic Energy Commission through Contract No. AT(30-1)-1922.

(1) R. COLL, R. NAUMAN and P. WEST, *J. Amer. Chem. Soc.* **81**, 1284 (1959).
(2) G. BOYD and S. LINDENBAUM, Abstracts of papers presented at the 134th Meeting of the American Chemical Society, p. 18-I Chicago (1958).

EXPERIMENTAL

Material. High activity ^{59}Fe and ^{114}In were obtained from Oak Ridge National Laboratory in the form of ferric and indium chloride, respectively, each in hydrochloric acid solution. Dinonyl naphthalene sulphonic acid was the same as that used by WHITE *et al.*[2] Tri-n-octylamine was obtained from Eastman Organic Chemicals Co. An acid equivalence determination showed the sample to be 99 per cent pure. In order to transform the tertiary amine to its hydrochloric or perchlorate salt, a solution of it in benzene was equilibrated with an equal volume of 1 M hydrochloric or perchloric acid. The amine was light yellow in colour; its hydrochloride and perchlorate salts were light yellow and slightly pink, respectively, in benzene. Other chemicals were of reagent grade.

Procedure. In the liquid ion-exchange experiments the aqueous phase normally was prepared to contain metal ion (radioisotope) in concentration of the order of 10^{-7} M and varying concentrations of hydrochloric and/or perchloric acid. The benzene phase contained varying amounts of tri-n-octylamine hydrochloride as the liquid anion exchanger or dinonyl naphthalene sulfonic acid as the liquid cation-exchanger. The organic phase was always pre-equilibrated with an equal volume of the aqueous solution to be used, without the radioisotope.

Equal volumes of the aqueous and organic phases were mixed in glass-stoppered volumetric flasks, shaken at 25 ± 0·5° overnight and allowed to settle for 1hr. Aliquots of both phases were removed, and the activity of the metal ion in each phase was measured with a γ-ray scintillation well counter. The precision attained was generally better than 2 per cent. The distribution coefficient is defined by the equation

$$K_d = \frac{\text{total M(III) concn. in organic phase}}{\text{total M(III) concn. in aqueous phase}} \quad (1)$$

TABLE 1.—LIQUID CATION EXCHANGE EXPERIMENT WITH Fe(III) AT (HD) = 0·147 F, TOTAL ACID AT 1·00 M

HCl	$HClO_4$	K_d
0·00	1·00	3·01
0·20	0·80	1·60
0·40	0·60	1·10
0·50	0·50	0·93
0·60	0·40	0·78
0·80	0·20	0·65

RESULTS AND DISCUSSION

(A) *Liquid cation-exchange experiments with* Fe(III) *and* In(III)*–chloride complexes.* In each experiment the total hydrogen ion concentration was kept constant while the ratio of hydrochloric acid to perchloric acid varied. A typical experiment with Fe(III) at a total hydrogen ion concentration of 1·00 M is summarized in Table 1, and a plot of $1/K_d$ vs. (Cl^-) given in Fig. 1.

If we assume no complexation between M^{3+} and ClO_4^-, the K_d in the absence of hydrochloric acid may be taken to be equal to K_d°, and the method of WHITE *et al.*[3] used to calculate the stability constant K_1 for the reaction $M^{3+} + Cl^- = MCl^{2+}$.

The stability constants obtained for Fe(III) and In(III)–chloride with the use of dinonyl naphthalene sulphonic acid are summarized in Table 2, which also includes values taken from the literature for comparison.

From Table 2, it is obvious that the stability constant of $FeCl^{2+}$ complex at ionic strengths varying from 0·20 to 1·00 is independent of whether H^+ or Na^+ is the cation of the perchlorate ion. The specific ion effect on the stability of the $FeCl^{2+}$ complex

[3] J. WHITE, P. TANG and N. C. LI, *J. Inorg. Nucl. Chem.* **14**, 255 (1960).

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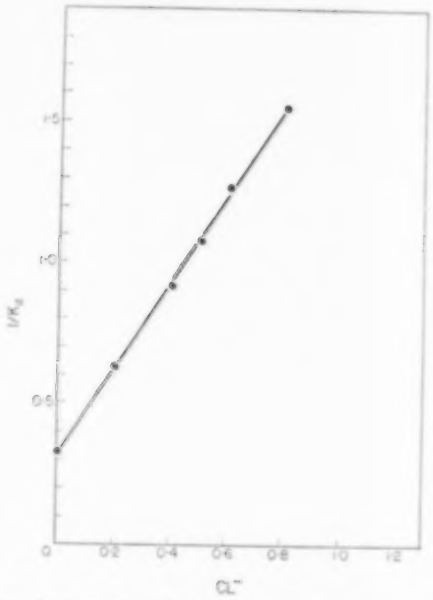

FIG. 1.—$1/K_d$ vs. Cl^-, for Fe(III) in HCl–$HClO_4$ mixtures. Total hydrogen ion concentration, 1 M.

TABLE 2.—STABILITY CONSTANTS OF Fe(III) AND In(III)–CHLORIDE COMPLEXES, 25°

Method	Total ionic strength	Maintained by	log K_1	Ref.
(a) Fe(III)–chloride complex				
Liq. cation exchange	0·20	HCl, $HClO_4$	0·78	+
Spectrophotometric	0·20	HCl, $NaClO_4$	0·77	4
Liq. cation exchange	0·30	HCl, $HClO_4$	0·71	+
Spectrophotometric	0·30	HCl, $NaClO_4$	0·70	4
Liq. cation exchange	1·00	HCl, $HClO_4$	0·66	+
Spectrophotometric	1·00	HCl, $NaClO_4$	0·62	4
(b) In(III)–chloride complex*				
Liq. cation exchange	1·00	HCl, $HClO_4$	2·52	+
Resinous ion-exchange	1·00	$NaClO_4$	2·18 (20°)	5
Solvent extraction	1·00	$NaClO_4$	2·20 (20°)	6
Liq. cation exchange	2·00	HCl, $HClO_4$	2·51	+
Electromotive force	2·00	$NaClO_4$	2·15 (20°)	6(*b*)

* This investigation
† Concn. range of HCl: 0–0·09 M
[4] E. RABINOWITCH and W. STOCKMAYER, *J. Amer. Chem. Soc.* **64**, 335 (1942).
[5] N. SUNDEN, *Svensk Kem. Tidskr.* **66**, 173 (1954).
[6] N. SUNDEN, *Svensk Kem. Tidskr.*[a] **66**, 345 (1954); [b] **66**, 20 (1954).

found by COLL *et al.*[1] above 5 M, therefore, is absent at these lower ionic strengths.

For In(III)–chloride complex, however, the substitution of Na^+ for H^+ as cation of the perchlorate ion decreases the log K_1 by about 0·3 at ionic strengths of one and two. Since In(III)–chloride complex is much more stable than Fe(III)–chloride complex, it is not surprising to find that the specific ion effect begins to be noticeable at a much lower ionic strength for In(III) than for Fe(III).

COZZI and VIVARELLI[7], using a polarographic method in a 2 M sodium perchlorate medium, obtained log $K_1 = 4{\cdot}30$ for the $InCl^{2+}$ complex. However, the limiting polarographic current obtained was partly of a kinetic nature and the polarographic electrode reaction therefore is not strictly reversible. For this reason, the polarographic stability constant value is probably too high and is not included in Table 2.

(B) *Liquid anion-exchange experiments with* Fe(III) *and* In(III)*–chloride complexes.* The purpose of this series of experiments was to determine the existence of negatively-complexes of Fe(III) and In(III) with chloride in either the aqueous or organic phase.

The equilibration of tri-n-octylamine in benzene with aqueous hydrochloric acid or perchloric acid and back titration of the organic phase with standard sodium hydroxide showed that no significant amount of the extractant was scrubbed out into the aqueous phase and that one equivalent of TOA combines with one equivalent of hydrochloric or perchloric acid, so that the species R_3NHCl or R_3NHClO_4 is formed in benzene. This is in contrast to the behaviour of nitric acid noted by CARSWELL and LAWERNCE[8] who reported that more than one equivalent of nitric acid will associate with one equivalent of the TOA in the organic phase, and that the concentration of nitric acid dissolved in the amine–nitrate compound is a linear function of both nitric acid and amine–nitrate concentrations in the aqueous and organic phases, respectively.

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The simplest generalized equation for the extraction of ferric or indium chloride can be written as follows

$$M_a^{3+} + 3\,Cl_a^- + n\,R_3NHCl = (R_3NH)_nMCl_{3+n} \qquad (2)$$

where the subscript *a* denotes the aqueous phase and no subscript denotes the organic phase. The corresponding mass law expression, in terms of concentrations rather than activities, is:

$$K = ((R_3NH)_nMCl_{3+n})/(M^{3+})_a(Cl^-)_a{}^3(R_3NHCl)^n \qquad (3)$$

Among the simplifying assumptions made are that the amine hydrochloride exists as a monomeric species,* that a single extracted species of complex is formed, and that the activity coefficients of the various species are essentially unchanged.

* This is by analogy with the thought of KEDER *et al.*[6b] that the species formed upon equilibration of an amine solution with nitric acid is $Octyl_3NH^+\,NO_3^-$. Although COLEMAN *et al.*[8c] postulate that the amine salts associate into aggregates, they themselves state that direct evaluation of the average molecular weights by light scattering and by isopiestic osmotic balancing shows that not all of the amine salts concerned are aggregated. Moreover, COLEMAN's hypothesis of the polymeric nature of the amine salts was based on the finding that the uranium extraction coefficients vary with approximately the first power of the extractant concentration, which is not the case for the ferric and indium distribution coefficients investigated in the present study.

[7] D. COZZI and S. VIVARELLI, *Z. Elektrochem.* **57**, 408 (1953); *Chem. Abstr.* **48**, 1870^e (1954); J. J. BJERRUM, G. SCHWARZENBACH and L. G. SILLÉN, *Stability Constants, Special Publication No.* 6, *Part* I: *Organic Ligands.* The Chemical Society, London (1957).

[8a] D. CARSWELL and J. LAWRENCE, *J. Inorg. Nucl. Chem.* **11**, 69 (1959); [b] W. E. KEDER, J. C. SHEPPARD and A. S. WILSON, *Ibid.* **12**, 327 (1960); [c] C. F. COLEMAN, K. B. BROWN, J. G. MOORE, and D. J. CROUSE, *Industr. Engng. Chem.* **50**, 1756 (1958).

In view of equation (1), the distribution coefficient is given by the equation

$$K_d = \frac{((R_3NH)_nMCl_{3+n})}{(M^{3+}) + (MCl^{2+}) + (MCl_2^{+}) + \ldots} \tag{4}$$

By introducing the term $K_i = (MCl_i)/(MCl_{i-1})(Cl^-)$, equation (4) may be written

$$K_d = \frac{((R_3NH)_nMCl_{3+n})}{(M^{3+})(1 + K_1(Cl^-) + K_1K_2(Cl^-)^2 + \ldots)} \tag{5}$$

Equation (3) therefore may be rearranged to give

$$K_d = \frac{K\,(Cl^-)^3\,(R_3NHCl)^n}{1 + K_1\,(Cl^-) + K_1K_2\,(Cl^-)^2 + \ldots} \tag{6}$$

According to equation (6), at constant concentration of chloride ion, n can be determined from a plot of log K_d vs. log (R_3NHCl).

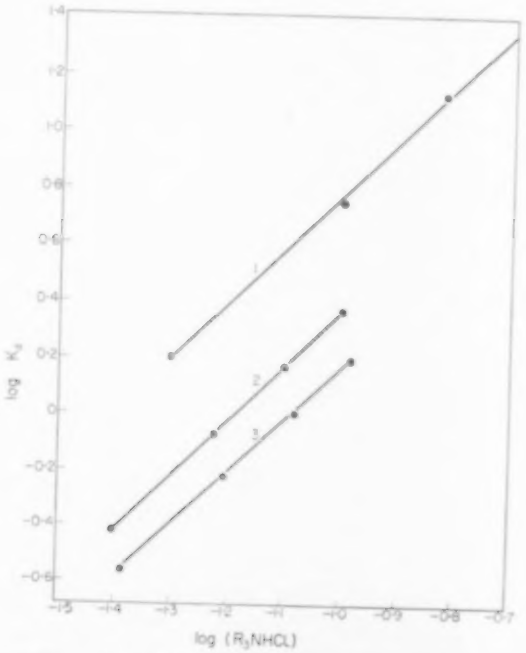

FIG. 2.—Dependency, tri-n-octylamine hydrochloride concentration on the extraction of Fe(III) and In(III) from chloride media.
Curve 1: Fe(III) in 0·971 M HCl, slope = 1·94.
Curve 2: Fe(III) in the medium 0·241 M HCl, 0·60 M NaCl, slope = 1·98.
Curve 3: In(III) in 1·319 M HCl, slope = 1·87

A test of the dependency of the extraction of Fe(III) and In(III) on the concentration of R_3NHCl was made by varying the amine concentration at constant total chloride ion concentration. The results are summarized in Fig. 2. The value of n is determined to be two, so that the negatively charged $FeCl_5^{2-}$ and $InCl_5^{2-}$ complexes are formed in the organic phase.

Direct evidence for the nature of the highest complex formed is not easy to obtain.

By combining solvent extraction and absorption spectra, NACHTRIEB and CONWAY[9] stated that the ferric-chloro complex extracted from solutions containing above 8 M HCl into isopropyl ether, may possibly be interpreted as evidence for the formation of higher complexes of formula H_2FeCl_5, H_3FeCl_6, etc., or as a salting-in effect caused by $FeCl_3$. This investigation however, is the first to give positive evidence that the negatively charged $FeCl_5^{2-}$ and $InCl_5^{2-}$ complexes are formed in the organic phase, in the form $(R_3NH)_2MCl_5$.

Table 3 lists the results obtained in the extraction of Fe(III) and In(III) by 0·10 M tri-n-actylamine hydrochloride at varying hydrochloric acid concentrations.

TABLE 3.—EXTRACTION OF M(III) BY 0·10 M TRI-N-OCTYLAMINE HYDROCHLORIDE

(a) Fe(III)			(b) In(III)		
HCl (M)	K_d	K_d calc.	HCl (M)	K_d	K_d calc.
0·245	0·25	0·24	0·331	0·24	0·33
0·344	0·51	0·54	0·428	0·32	0·44
0·443	0·93	0·99	0·466	0·35	0·48
0·540	1·58	1·57	0·526	0·43	0·54
0·640	2·52	2·31	0·624	0·51	0·64
0·738	3·61	3·17	0·721	0·65	0·75
			0·737	0·63	0·76
			0·819	0·78	0·85
			1·008	0·96	1·05
			1·279	1·40	1·35

For Fe(III)–chloride complex, since Fig. 1 shows that a plot of $1/K_d$ vs. (Cl^-) is linear, the value of K_2 is negligible so that the third term in the denominator of equation (6) may be dropped. A plot of K_d vs. $(R_3NHCl)^2$, at constant chloride ion concentration, would be linear with zero intercept and K may be calculated from the equation

$$K_d = \frac{K\,(Cl^-)^3\,(R_3NHCl)^2}{1 + 10^{0.66}\,(Cl^-)} \qquad (7)$$

From the data of Fig. 2, curve 1 (extraction of Fe(III) at constant concentration of 0·971 M HCl), and taking $K_1 = 4{\cdot}6$ from Table 2, the value of K has been calculated to be 3200.

The In(III) chloride complex is very much more stable than the Fe(III) chloride complex, and linear plots of $1/K_d$ vs. (Cl^-) were obtained only in chloride concentration range up to 0·09 M, when the liquid cation exchanger, dinonyl naphthalene sulphonic acid, was used. In the liquid anion-exchange experiments however, hydrochloric acid concentration up to 1·3 M was used, so that the presence of $InCl_2^+$ complex has to be considered, and therefore all three terms in the denominator of equation (6) have to be used. In 1 M sodium perchlorate medium, SUNDEN[6] has found for In–Cl system: $\log K_1 = 2{\cdot}20$, $\log K_2 = 1{\cdot}36$. Since our value of $\log K_1$, 2·52, is higher by 0·32 than SUNDEN's value the difference being ascribed to the specific ion effect, we may ascribe the same magnitude of the specific ion effect to K_2, and assume $\log K_2 = 1{\cdot}68$.

[9] N. H. NACHTRIEB and J. G. CONWAY, *J. Amer. Chem. Soc.* **70**, 3547 (1948).

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Equation (6) thus becomes

$$K_d = \frac{K\,(Cl^-)^3\,(R_3NHCl)^2}{1 + 10^{2\cdot52}\,(Cl^-) + 10^{2\cdot52}\,10^{1\cdot68}\,(Cl^-)^2} \qquad (8)$$

From the data of Fig. 2, curve 3 (extraction of In(III) from a constant concentration of 1·319 M HCl), we have obtained a linear plot of K_d vs. $(R_3NHCl)^2$. The slope of the straight line is 139, from which K is calculated to be $1{\cdot}69 \times 10^6$. The stability of the $InCl_5^{2-}$ complex in the organic phase (equations 2 and 3) is therefore very much greater than the $FeCl_5^{2-}$ complex in the organic phase.

From equations (7) and (8), it is obvious that for Fe(III), K_d at constant concentration of R_3NHCl, would be between second and third power dependent on the chloride

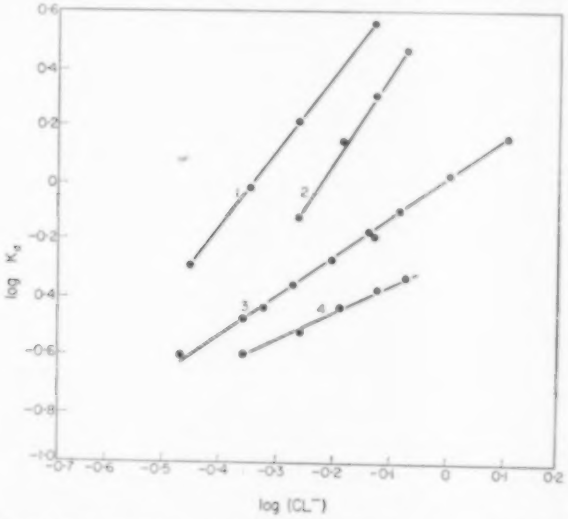

FIG. 3.—Dependency, chloride concentration on the extraction of Fe(III) and In(III).
Curve 1: Fe(III) in HCl only; R_3NHCl, 0·109 M
Curve 2: Fe(III) in HCl–NaCl mixtures (HCl constant at 0·241 M); TOA HCl, 0·109 M
Curve 3: In(III) in HCl only; R_3NHCl, 0·104 M
Curve 4: In(III) in HCl–NaCl mixtures (HCl constant at 0·241 M); TOA HCl, 0·100 M.

ion concentration, while for In(III), the corresponding dependence would be between first and second power. These conclusions have been confirmed from plots of log K_d vs. log (Cl^-) given in Fig. 3, curves 1 and 3. The slopes of curves 1 and 3 are 2·54 and 1·35 for Fe(III) and In(III), respectively.

In columns 3 and 6 of Table 3 are listed the values of K_d, calcd. for Fe(III) and In(III), respectively. These were calculated by means of equations (7) and (8), with $K = 3200$ for Fe(III) and $K = 1{\cdot}69 \times 10^6$ for In(III). The agreement between the observed and calculated K_d shows that the generalized equation for the extraction of Fe(III) and In(III), (equation 2), and its underlying assumptions are essentially correct.

Fig. 2, curve 2 and Fig. 3, curves 2 and 4 show the results obtained on the extraction of Fe(III) and In(III) from HCl–NaCl mixtures. The distribution coefficients from such mixtures are always lower than from HCl of the same total chloride ion concentration. Since the activity coefficients in HCl–NaCl mixtures are known to deviate from

those in pure HCl solutions,[10] and since the stability constants of the ferric and indium–chloride complexes are not known in HCl–NaCl mixtures, no attempt at quantitative evaluation of data in HCl–NaCl mixtures can be made at this time.

With perchloric acid as the aqueous medium, up to 2 M, and no chloride present, all of the ^{59}Fe or ^{114}In activity remained in the aqueous phase. Since there is no extraction into the organic phase, we may conclude that the perchlorate ion does not form a negatively charged complex with Fe(III) or In(III) in the organic phase.

[10] R. A. ROBINSON and R. H. STOKES, *Electrolyte Solutions* p. 422. London (1955).

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J. Inorg. Nucl. Chem., 1961, Vol. 16, pp. 345 to 349. Pergamon Press Ltd. Printed in Northern Ireland

ION EXCHANGE IN MIXED SOLVENTS—IV

THE DISTRIBUTION OF THORIUM BETWEEN ALCOHOL–NITRIC ACID SOLUTIONS AND THE STRONGLY-BASIC ANION EXCHANGER DOWEX-1. SEPARATION OF THORIUM FROM URANIUM

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(*Received* 18 *May* 1960)

Abstract—The present work was carried out in order to develop a rapid and accurate means of separating thorium and uranium. Experiments have shown that the adsorption of thorium as a negatively-charged nitrate complex on strongly-basic anion exchangers from solutions containing aliphatic alcohols and nitric acid is very high compared with its adsorption from pure nitric acid solutions devoid of any organic solvent. After determining the distribution coefficients of thorium and uranium in nitric acid solutions containing aliphatic alcohols it was possible to develop a method for the separation of thorium from uranium by means of anion exchange.

IN continuation of the work of ANTAL *et al.*[1] on the distribution of thorium, zirconium and titanium between mineral acid–alcohol solutions and the strongly-basic anion exchanger Dowex-1, we have determined the adsorption of thorium from nitric acid solutions containing aliphatic alcohols, viz. methanol, ethanol, propanol, butanol etc.

Since uranium is only very weakly adsorbed under conditions where thorium shows a very high distribution coefficient, the separation of these two elements by means of a column operation using Dowex-1 can easily be carried out. In addition, the resin shows a very high affinity for thorium, so that the quantitative separation of both microgram and milligram quantities of thorium from much larger amounts of uranium becomes possible.

In earlier papers[2,3] we have reported the distribution of uranium between mineral acid–alcohol solutions and Dowex-1, as well as the adsorption of thorium tetrachloride on Amberlite IRA–400 and Dowex-1.[3] In these papers the probable reasons for the stronger adsorption of many elements from their mineral acid–alcohol solutions on strongly-basic anion exchangers compared with their behaviour in solutions of pure mineral acids were mentioned. The alcohols seem also to exert a complexing effect on thorium, the magnitude of which decreases with increasing chain length of the alcohol molecule.

The use of alcoholic solvents containing hydrochloric or nitric acid has already found practical analytical application for the determination of uranium[4] and thorium[5] in minerals and rocks.

EXPERIMENTAL

Solutions and reagents

Air-dried Dowex 1-X 8 (100–200 mesh nitrate form) was used. The aliphatic alcohols (methanol, ethanol, n-propanol, n-butanol and a mixture of the amyl alcohols) were reagent grade

[1] P. ANTAL, J. KORKISCH and F. HECHT, *J. Inorg. Nucl. Chem.* **14**, 247 (1960).
[2] J. KORKISCH, P. ANTAL and F. HECHT, *J. Inorg. Nucl. Chem.* **14**, 253 (1960).
[3] J. KORKISCH and F. TERA, *J. Inorg. Nucl. Chem.* **15**, 177 (1960).
[4] J. KORKISCH, P. ANTAL and F. HECHT, *Z. Anal. Chem.* **172**, 401 (1960).
[5] J. KORKISCH and P. ANTAL, *Z. Anal. Chem.* **171**, 22 (1959).

solvents. The standard solutions of thorium and uranium contained the reagent grade nitrates of these elements dissolved in 5 N nitric acid. Thorium was determined quantitatively with thoronal (0·1% aqueous solution),[6] using a Beckman model B spectrophotometer. The absorbance measurements were carried out in 1 cm cells at 545 mμ using a blue-sensitive photo-cell.

The column operations were carried out in columns of the same type and dimensions as those described earlier.[7]

Quantitative determination of thorium and uranium

The method used for the quantitative determination of thorium is exactly the same as that described in an earlier paper.[3]

Uranium determinations in the effluents or in the filtrates after removing the resin were carried out in the following manner.

An aliquot was transferred to a quartz dish, and the solution was evaporated to dryness on a water bath. The residue was then ignited to remove organic matter. After cooling to room temperature about 10 ml of 4–6 N hydrochloric acid were added and the solution was evaporated to dryness once more. The residue was then taken up in 10 ml 0·01 N nitric acid and the uranium was determined polarographically utilizing the catalytic nitrate wave.[4,7]

Determination of distribution coefficients

Distribution coefficient K_d were always determined in a volume of 25 ml. For mixtures containing 99 per cent alcohol, 1 ml of thorium or uranium standard solution (5,000 μg Th or 250 μg U dissolved in 5 N nitric acid) was evaporated in a conical flask to complete dryness. The residue was then dissolved in 0·25 ml 5 N nitric acid and 24·75 ml of the alcohol was added. Similarly 1 ml of the standard solution and 24 ml alcohol gave a mixture which contained 96 per cent alcohol. All other solutions containing different percentages of alcohol were prepared in a similar manner. In the case of amyl alcohol two definite layers were formed at less than 80 per cent alcohol so that in this case distribution coefficients were only recorded at higher alcohol concentrations (see Fig. 1).

After preparing the solutions, 1 g of resin was added to each solution, and the stoppered flasks were shaken thoroughly on a shaking machine for 24 hr. The resin was then filtered off, and the thorium or uranium was determined in the filtrate as described above.

The results shown in Figs. 1–3 have been obtained using the procedure described above.

Column operations (separation of thorium from uranium)

After pretreating the resin bed with 50 ml 90 per cent methanol-mixture (5 ml 5 N nitric acid + 45 ml methanol) the sorption solution (90 ml methanol and 10 ml 5 N nitric acid) containing the thorium and uranium was passed through the column at a flow-rate not exceeding 50 ml/hr. The uranium stays in solution and the thorium is adsorbed on the resin. The column was then washed at the same flow-rate with 250 ml of 90 per cent methanol-acid solution to remove the last traces of uranium from the resin. Afterwards, the thorium was eluted with 100 ml 1 N nitric acid. All separations of thorium from uranium were completely quantitative (Table 1), due to the fact, that the distribution coefficient for thorium in this medium is 12,475 whereas that for uranium is only about 34. In one experiment uranium (500 mg) was passed through the column in the absence of thorium and the operation was performed in the manner described above. A uranium determination on the eluate showed that less than 1 μg U has been adsorbed by the resin, i.e. the separation of uranium from thorium is completely quantitative.

RESULTS

Fig. 1 shows the effect of the alcohol concentration on the distribution coefficient K_d, which is given by the following equation:

$$K_d = \frac{\mu\text{g thorium/g resin}}{\mu\text{g thorium/ml solution}}$$

[6] J. KORKISCH and P. ANTAL, *Z. Anal. Chem.* **173**, 126 (1960).
[7] J. KORKISCH, A. FARAG and F. HECHT, *Mikrochim. Acta* (Wien) 415 (1958).

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The curves show that the adsorption of the thorium nitrate complex on the resin is highest in a methanolic and lowest in an amyl alcoholic medium. This effect is reversed when hydrochloric acid is used instead of nitric acid, e.g. the adsorption of thorium from methanol–HCl solution is very low.[3] From Fig. 1 it is also clear that the thorium adsorption from a nitric acid–alcohol solution decreases with increasing length of the carbon chain in the alcohols concerned. Secondary alcohols such as iso-propyl and sec-butyl alcohol have been found to behave like the corresponding

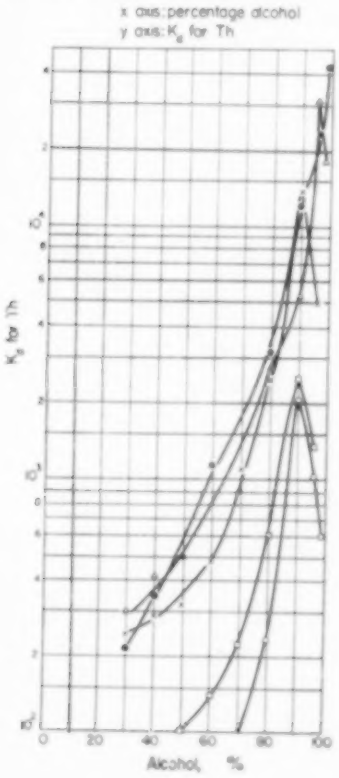

FIG. 1.

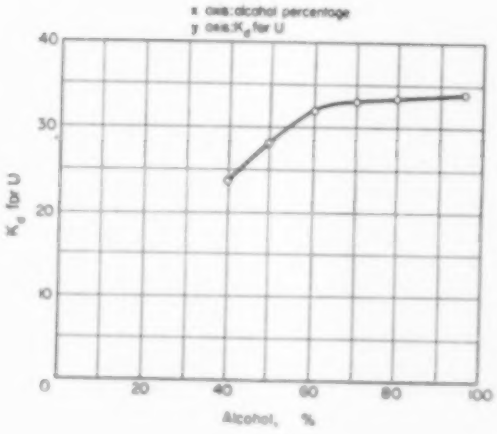

FIG. 2.

normal alcohols. In 99 per cent solution K_d for n-propyl alcohol and n-butyl alcohol is only 25 and 10 respectively.

Since thorium shows the highest distribution coefficient in methanol solutions, values of K_d for uranium were measured in this medium only (Fig. 2). This curve shows that the distribution coefficient is very low at all alcohol concentrations and only attains a value of 34 in 96 per cent methanol.

The effect of nitric acid concentration on the percentage of adsorbed thorium was also investigated in solutions containing 5 mg thorium and 96 per cent methanol. The results showed that the acidity of the solution has no influence on the adsorption of the negatively-charged thorium nitrate complex. In the range from 0·6 N to 0·005 N no hydrolysis occurs, and 4,997 μg thorium out of 5,000 μg are adsorbed on the resin in each case. At 0·0025 N acid the thorium nitrate is partly hydrolysed, and the

solution becomes turbid; more than 90 per cent of the thorium remains in solution on equilibration with the resin. In hydrochloric acid–alcohol solution partial hydrolysis takes place at 0·04 N acid.[3] These results show that the negatively-charged chloride complex of thorium is less stable and less strongly adsorbed than the nitrate complex.

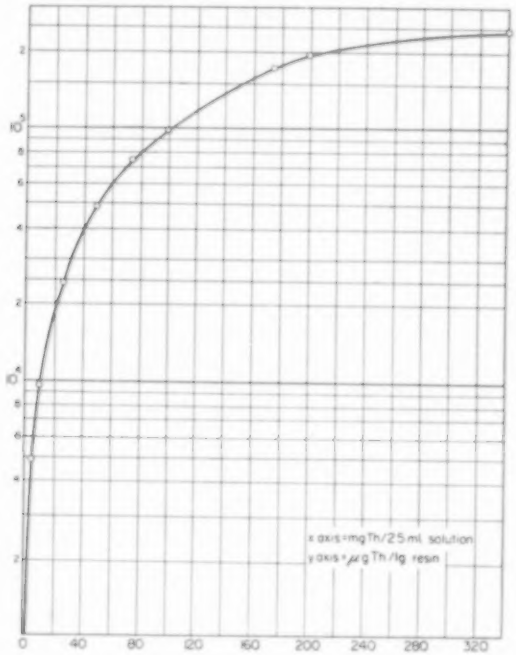

FIG. 3.

TABLE 1

Thorium used (μg)	Uranium used (mg)	Thorium found (μg)	Uranium found (mg)
0	500	0	500
100	500	105	500
100	50	100	50
100	5	108	4·98
100	1	100	0·994
100	0·1	100	0·0994
10	25	9·5	25
1000	1	1012	0·986

Fig. 3 shows the adsorption isotherm at room temperature in 90 per cent methanol, *i.e.* under the conditions used for the separation of thorium from uranium. This shows that up to 200 mg thorium/25 ml solution, practically 100 per cent adsorption takes place. The total exchange capacity of the resin in 90 per cent methanol is 3·96 mg equiv./g dry resin (nitrate form).

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Separation of thorium from uranium

Table 1 records the results of a series of experiments showing that the separation of these two elements is completely quantitative, expected from the results shown in Figs. 1 and 2.

Since small changes in the percentage of methanol and even great changes of acidity do not greatly affect the distribution coefficients of thorium and uranium, we can completely neglect loss of methanol by evaporation, and even relatively high changes in acidity. The flow-rate and the volume of wash solution are also not critical, and treatment of the column with twice or three times the volume of wash solution does not affect the results.

Since many other elements behave under these conditions in the same way as either thorium or uranium, this work will be extended.

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RADIOMETRIC AND AMPEROMETRIC TITRATIONS OF COPPER WITH t-ANTHRANILIC ACID*

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(*Received* 13 *June* 1960)

Abstract—A method of analysis in which metal ions are titrated radiometrically with tritium-labelled organic analytical reagents has been developed, using the copper–anthranilic acid system as an example. Amperometric titrations were carried out to establish optimum conditions for the precipitation titration. Radiometric and amperometric end-points were found to be identical and reproducible. A technique is suggested for the routine analysis of metal ions, with tritium-labelled organic reagents.

RADIOMETRIC titrations using labelled inorganic ions are now well established. The first of these was performed by LANGER[1], who used phosphorus-32 for titrations of metal ions with labelled phosphate. MOELLER *et al.*[2] have reviewed the general methods of radiometric titrations and have employed silver-111 and sulphur-35 for the titration of halogens and sulphate respectively, whilst DUNCAN and THOMAS[3] have used dithizone in solvent-extraction titrations of cobalt-60 and other radioactive transition metals.

The use of tritium-labelled anthranilic acid in the radiometric titration of copper is reported in this paper. The results of preliminary experiments were published in an earlier communication.[4]

Owing to the large dilution factor involved in radiometric titrations of this type, it is necessary to work with compounds of relatively high specific activity. This has not previously been possible with organic reagents but the recently-developed WILZBACH technique[5] for the tritiation of organic compounds in a single-stage process provides a method of obtaining specific activities high enough for use in radiometric titrations.

Since there is a considerable potential for tritium-labelled organic reagents in analytical chemistry, the term "Tritiometry" is proposed for this type of radiometric titration in accordance with MELLON's suggestion[6] that analytical nomenclature should consistently identify procedures by the characteristic property involved.

Anthranilic acid was chosen because of the ease with which it can be labelled with tritium. BROWN and GARNETT have shown[7] that the tritiation of a simple aromatic compound proceeds more efficiently and produces less decomposition products than

* Presented, in part, at the 204th Meeting of the University of Sydney Chemical Society, November, 1959.
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[1] A. LANGER, *J. Phys. Chem.* **45**, 639 (1941)
[2] D. W. MOELLER, J. G. TERRILL and M. S. SEAL, *Proceedings of the International Conference on the Peaceful uses of Atomic Energy, Geneva*, 1955, P/233, Vol. 15, p. 49. United Nations (1956)
[3] J. F. DUNCAN and F. G. THOMAS, *J. Inorg. Nucl. Chem.* **4**, 376 (1957).
[4] G. H. AYLWARD, J. L. GARNETT, J. W. HAYES and S. W. LAW, *Chem. & Ind.* 560 (1960).
[5] K. E. WILZBACH, *J. Amer. Chem Soc.* **79**, 1013 (1957).
[6] M. G. MELLON, *Quantitative Analysis* p. 555. Cromwell New York, (1955)
[7] W. G. BROWN and J. L. GARNETT, *J. Appl. Rad. Isotopes* **5**, 114 (1959).

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that of an aliphatic compound or a complex aromatic compound. Since anthranilic acid is not a very satisfactory reagent for the volumetric estimation of copper, the method described in this paper is not proposed as a practical analytical procedure but is presented as an illustration of a general technique applicable to metal ion analysis.

The amperometric method of detecting the end-point was used in this investigation to establish the optimum conditions for the radiometric titration, and also served to standardise the organic reagent.

EXPERIMENTAL

Amperometric titrations. Titrations were performed in a cell of 50 ml capacity similar to that designed by HUMAN and LEACH[8]. The applied voltage was regulated by a conventional polarizing unit.[9] A dropping mercury electrode was used as the cathode and a saturated calomel electrode of the BRUNNER and MEANS[10] type as the anode.

The polarogram of copper in 0·1 M acetate and 0·002 per cent Triton X-100 shows a well-defined step in the vicinity of 0·0 V versus the saturated calomel electrode, whilst sodium anthranilate is not reduced at the dropping mercury electrode in this supporting electrolyte. Consequently an applied e.m.f. of −0·5 V versus the saturated calomel electrode was chosen for the amperometric titrations.

Prior to the titration the solution was deoxygenated by passing nitrogen for 10 min. The titrant (0·17 M sodium anthranilate solution) was added from a 10 ml burette in steps of 0·2–0·4 ml. Nitrogen was passed through the solution to mix the contents of the cell, and the current reading was taken after allowing a suitable time for the diffusion layer to build up around the dropping mercury electrode. The volume of titrant was plotted against the diffusion current and the lines of best fit were drawn in the usual manner. Volume correction was found to be unnecessary.[9]

Radiometric titrations. The cell used for amperometric titrations was modified for radiometric titrations by removing the dropping mercury electrode and inserting a filter stick (porosity No. 3) connected to a manifold to which either nitrogen pressure or vacuum could be applied (Fig. 1). In this way the precipitated copper anthranilate could be separated from the supernatant liquor for sampling and the excess supernatant liquor could then be returned to the cell. Triplicate samples (ca. 3–5 mg) of the supernatant liquor from the titration mixture were taken by means of a 0·1 ml blood pipette and placed in tared ampoules which were sealed and reweighed.

Radiometric titrations were performed by two different procedures on 3 mM and 1·5 mM copper solutions. The first (A) resembled the method used in the amperometric experiments and involved successive additions of 0·2–0·4 ml increments; sampling was carried out approximately 45 min after each addition. The time interval between successive additions was dictated by the rate at which the ampoules for tritium analysis could be weighed on the microbalance. In the second procedure (B), an excess of titrant was added and sampling was carried out at one point only after a suitable lapse of time (20 min). In procedure A the solution was mixed by passing nitrogen and in Procedure B by stirring with a mechanical stirrer. The titrations were performed in artificial light to minimise decomposition of the sodium anthranilate solution. The specific activities of the titrants used were 2·6 and 4·0 mc/mM respectively.

Tritium assay. This was performed using a modification[11] of the method of WILZBACH *et al.*[12] In cases where the sample weight was less than 4 mg, an ampoule containing water was added to the combustion tube to bring the total liquid weight up to approximately 5 mg. Propane was used as counting gas instead of methane as originally recommended.[13]

Reagents. Analytical reagent grade chemicals (with the exception of anthranilic acid) were used throughout these experiments. Commercial (May and Baker) anthranilic acid was recrystallised four times from hot water to constant melting point (145°C)[14] using activated alumina as absorbent.

[8] J. P. E. HUMAN and S. J. LEACH, *Chem. & Ind.* 149 (1956).
[9] I. M. KOLTHOFF and J. J. LINGANE, *Polarography* (2nd Ed.) Ch. 47, Interscience, New York (1952).
[10] A. H. BRUNNER and P. B. MEANS, *Analyt. Chem.* **23**, 1525 (1951).
[11] J. L. GARNETT and S. W. LAW, *Aust. J. Chem.* in press
[12] K. E. WILZBACH, L. KAPLAN and W. G. BROWN, *Science* **118**, 522 (1953).
[13] K. E. WILZBACH, A. R. VAN DYKEN and L. KAPLAN, *Analyt. Chem.* **26**, 880 (1954).
[14] D. H. ANDREWS, G. LYNN, J. JOHNSTON, *J. Amer. Chem. Soc.* **48**, 1274 (1926).

The purified anthranilic acid was tritiated by the method of WILZBACH[5] and purified by recrystallization to constant specific activity.[11] Sodium hydroxide was added in stoichiometric proportion to a suspension of the acid in water and the mixture was stirred until the material was completely dissolved.

RESULTS AND DISCUSSION

Amperometric titrations. In agreement with ZHDANOV *et al.*[15] values of pH above 3·5 were found to be suitable for the titration (0·1 M acetate–acetic acid buffer in 16 per cent ethanol). However, contrary to the results of these workers the present

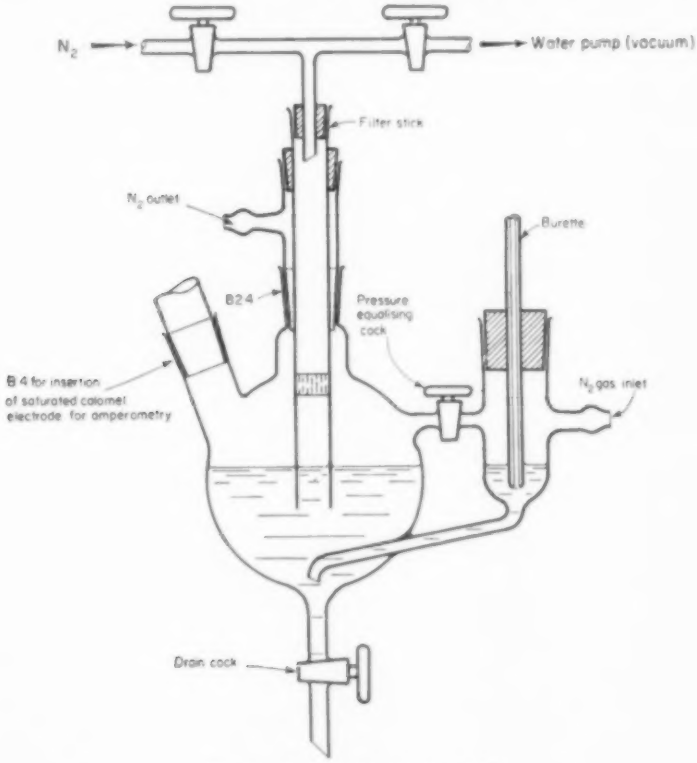

FIG. 1.—Radiometric titration cell.

authors found that increasing concentrations of supporting electrolyte produced a poorly-shaped titration curve and gave results which were considerably higher than expected. Furthermore, the concentration limit claimed by ZHDANOV *et al.*[15] could not be reproduced in 0·1 M supporting electrolyte (viz. 1·58 mg in 50 ml of solution ≡ 0·5 mM) but the lower limit was found to be 1·5 mM ± 1 per cent. This precision was possible only when an 8–10 min mixing time was allowed between the addition and the current reading. Titrations at lower copper concentrations were found to be impossible.

ZHDANOV *et al.*[15] reported that the titration can also be performed at an applied e.m.f. of 0·0 V versus the saturated calomel electrode, but the present authors could

[15] A. K. ZHDANOV, R. I. TSEITLIN and A. M. YAKUBOV, *Zavodskaya Lab.* **21**, 7 (1955).

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not obtain accurate results under these conditions. At this e.m.f. the copper step does not exhibit its limiting current.

Table 1 shows the results obtained at different concentrations of copper. Estimation of the precision was complicated by the decomposition of the sodium anthranilate solution. Each observed end-point is compared with the value calculated from the results obtained at a concentration of 3 mM.

TABLE 1.—RESULTS OF AMPEROMETRIC TITRATIONS

Cu (mM)	Obs. end-point (ml)	Calc. end-point (ml)
7·2	4·66	4·66
6·0	3·86	3·88
4·2	2·70	2·72
3·0	1·94	1·94
1·8	1·16	1·16
1·6	1·05	1·04
1·5	0·94	0·97
1·2	0·92	0·78

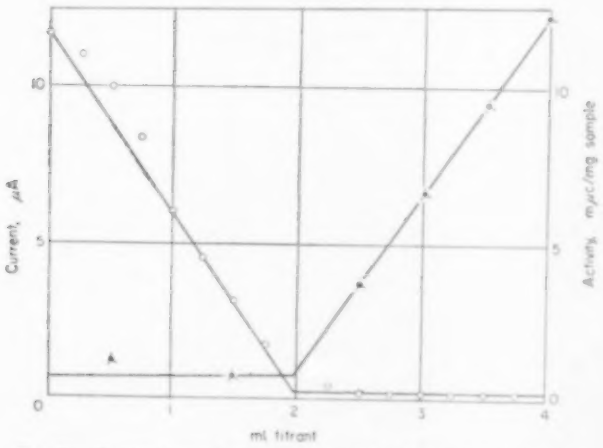

FIG. 2.—Comparison of amperometric and radiometric titrations.

The initial points of the titration curve do not fall on the linear portion of the graph (Fig. 2). The discrepancy between the non-linear and the linear portion of the curve may be attributed to :

(a) building up of an adsorption layer on the mercury surface during the initial stages of the titration,

or

(b) the kinetics of the reaction.

The technique of tensammetry[16] was used to investigate adsorption phenomena.

Sodium anthranilate solution in acetate buffer was found to exhibit a tensammetric

[16] B. BREYER and S. HACOBIAN, *Aust. J. Sci. Res.* A **5**, 500 (1952).

adsorption wave at about −1·2 V versus the saturated calomel electrode. However, when Triton X-100 was added to the system it was preferentially absorbed, and the wave due to anthranilate was eliminated. Since in the titrations Triton X-100 was present in constant amount (0·002 per cent) the deviation of the titration curve from the ideal cannot be attributed to this phenomenon.

When a longer mixing time was allowed between additions of reagent and reading the current, (up to 5 min) the currents in the initial stages decreased to a constant value which gave a more nearly linear plot. A much smaller change occurred in the currents on the linear portion of the graph with a resulting shift in the end-point of less than 0·5 per cent.

Table 2.—Results of radiometric titrations

Procedure	Approx. specific activity of Na Anthranilate (mc/mM)	Cu (mM)	Activity of sample (mμc/mg)	Radiometric end-point (ml)	Amperometric end-point (ml)
A	2·6	3·0		1·92	1·94
	2·6	3·0		1·94	1·94
	4·0	3·0		1·91	1·90
B	2·6	3·0	6·35	2·02	1·94
	2·6	1·5	10·09	1·17	0·97
	4·0	3·0	9·71	1·95	1·90
	4·0	3·0	9·57	1·98	1·90

These results indicate that the precipitation is slow, particularly in the initial stages. These findings are similar to those reported by Stock[17] for the copper–quinaldinic acid titrations. In agreement with his observations it was found that the reverse titration of copper with anthranilate facilitated the precipitation. However, the end-point was concordant with that obtained in the forward titration.

When 0·1 M potassium nitrate solution was used instead of acetate supporting electrolyte for the forward titration a slight improvement in the rate of formation of the precipitate was noted, but the reaction was still not instantaneous.

Radiometric titrations. Table 2 shows results for radiometric titrations using the two procedures. When the activities of the samples in millimicrocuries per milligram of sample (mμc/mg), corrected for increase in volume of the substrate,[9] were plotted against the volume of titrant added, a J-shaped curve was obtained.

However, an irregularity in the base-line was observed; initial points exhibited a higher activity than points closer to the end-point. This is analogous to the non-linearity of the initial portion of the amperometric curve. The slow rate of formation of the precipitate would explain the higher concentration of labelled species observed in the liquid phase in the early stages of the titration. From the data of the amperometric titrations the precipitation line for the radiometric titrations was drawn parallel to the axis through the point of lowest activity.

Good agreement was obtained between amperometric and radiometric titrations performed by Procedure A. In those cases where the titration was performed by Procedure B, agreement was not obtained with the amperometric end-points. In the

[17] J. T. Stock, *J. Chem. Soc.* 1793 (1949).

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latter procedure end-points were calculated on the assumption that the slope of the curve of activity versus volume of excess titrant would be identical to that obtained by Procedure A. It is considered that the discrepancy between the results of the two procedures can be attributed to different conditions of precipitation. It is still feasible that, provided standardisation were carried out, accurate estimations of copper could be made by the second technique.

The end-points of both amperometric and radiometric titrations carried out by Procedure A were consistently about 1·5 per cent higher than the stoichiometric relationship. It would be necessary, therefore, to standardise the sodium anthranilate under similar precipitation conditions.

CONCLUSION

The above results show that the use of tritiated organic analytical reagents for radiometric metal ion titration is feasible. Tritiometry experiments with more suitable analytical reagents are being performed in these laboratories. It would seem reasonable to suggest a method of routine metal ion analysis in which an excess of a tritiated organic reagent is added to a metal ion solution and after the lapse of a suitable time interval a sample of the supernatant liquor is taken and counted. This count could then be related to the original concentration of metal ion.

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NOTES

The rapid separation of ^{24}Na from ^{27}Mg

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In order to develop a method suitable for the separation and detection of radionuclides having a half-life of about 10–20 min, the separation of 14·9 hr ^{24}Na from 9·6 min ^{27}Mg was studied by us.

Several separations of sodium from magnesium are reported in the literature,[1–7] but since the problem is usually the isolation of long-lived ^{22}Na from deuteron-bombarded magnesium a rapid separation is not necessary. None of these seemed to us to be directly applicable to a rapid separation and a modification of the Samuelson–Sjöström method was therefore adopted, using a mixture of Dowex-2 in the free base and acetate forms.

The radioisotopes were produced by the nuclear reactions $^{27}Al(n,\alpha)^{24}Na$ and $^{27}Al(n,p)^{27}Mg$, using 14 MeV neutrons from a tritium target bombarded with deuterons from a 400 keV Cockcroft and Walton accelerator.

Since the separation procedure must operate in the presence of relatively large amounts of aluminium from dissolution of the irradiated target, the procedure was based on the inability of the resin to retain sodium and on the different stabilities of the EDTA complexes of magnesium and aluminium. At pH 7·5–8 both chelates are retained by the resin, but since the aluminium chelate remains stable over a wide pH range (3–10) while the magnesium chelate is less stable at the lower pH, the latter can be eluted from the resin with 1 N CH_3COOH. Before using the method on the sub-microgram scale, preliminary tests were carried out with synthetic feed solutions on the milligram scale to ensure that magnesium could be separated from aluminium without contamination despite the initial preponderance of the latter.

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Preliminary Experiments

In these a bed of Dowex-2, X-8 (100–200 mesh) was used, half in the hydroxyl form and half in the acetate form.

By tracing the feed with approximately 0·1 μc of ^{22}Na and plotting the effluent activity against the effluent volume, it was found that >98% of the sodium was contained in the first 25 ml. The magnesium recovery on elution with 1 N CH_3COOH was determined in the liquid collected after the first 25 ml from the above experiment and in three further experiments. The magnesium was estimated by complexometry after being absorbed on a small bed of Dowex 50-X-8 and eluted again. The recovery of magnesium was >98%.

By testing the magnesium-containing effluent with a standard solution of aluminium (0·02 M) with Chrom Azurol S as the indicator, it was shown that no appreciable amounts of EDTA salts were present. The presence of aluminium was checked in both the first 25 ml of effluent and the subsequent portion by back-titration of the EDTA-aluminium chelate with ferric ion; it was concluded that <2% of the initial amount of aluminium chelate (or other EDTA chelate) was present. Furthermore, the absence of aluminium ions in the latter portion of effluent was confirmed.

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[3] K. L. Hall, AECU–3126, 77 (1955).
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[6] O. Samuelson and E. Sjöström, *Analyt. Chem.* **26**, 1908 (1954).
[7] A. H. Heyn and H. L. Finston, *Analyt. Chem.* **32**, 328 (1960).

It was found that it is not convenient to use an amount of resin in the free base form higher than that corresponding to the number of equivalents of the anions contained in the feed solution; otherwise the residual free base resin tends to release gases when in contact with the 1 N acetic acid of the eluant.

Experiments on Irradiated Aluminium

(a) *Irradiation and radiochemical control*

Two aluminium foils, each of about 12 mg cm^{-2} and 54 mg, were irradiated in each experiment. The neutron flux through the target was $\sim 5{\cdot}3 \times 10^6$ neutrons cm^{-2} sec^{-1}. The irradiation time was 27 min, corresponding to the following predicted activities in each foil: 13 dis/sec ^{24}Na and $3{\cdot}55 \times 10^8$ d.p.s. ^{27}Mg. After irradiation, one of the foils was used for the chemical procedure described

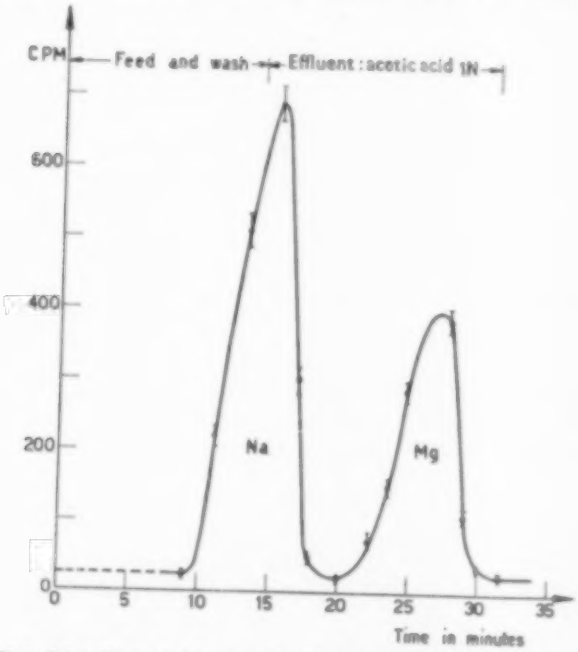

FIG. 1.—Plot of the effluent activity against time. The zero corresponds to the end of irradiation. Besides the ^{27}Mg peak, the ^{22}Na peak is present. ^{22}Na had been added to the feed.

below and the other for radiochemical control. The latter was carried out by introducing the aluminium foil into a standard γ-scintillation counter, fitted with a pulse height analyser, and determining the height of the photo-peak corresponding to the 0·834 MeV line in the γ-spectrum of ^{27}Mg. The decrease in the photo-peak hieght with time corresponded to the half-life of ^{27}Mg, and the absolute activity extrapolated to zero time was $3{\cdot}5 \times 10^3$ dis/sec in good agreement with the calculated magnesium activity at the end of the irradiation. The γ-scintillation counter detector was calibrated by means of the 0·84 MeV γ-peak of a standard ^{54}Mn source.

(b) *Chemical treatment and separation*

The second foil was rapidly dissolved in 1 ml of 6 N HCl with gentle warming. As soon as the metal was completely dissolved, the stoicheiometric amount of the disodium salt of EDTA was added as a boiling solution. After cooling, ammonium hydroxide was added to adjust the pH to $\sim 7{\cdot}5$. In this way, approximately 22 ml of active solution were obtained, which were fed to the resin at a rate of 2·5 ml min^{-1} cm^{-2}. The effluent samples (8 ml) were collected in glass tubes by means of an automatic sample changer. The column (2·1 cm^2 × 9·5 cm) contained Dowex-2, X-8

(100–200 mesh), 8 ml in the free base from and 12 ml in the acetate form, and a high-efficiency halogen-quenched G.M. liquid-flow counter[8] was used to monitor the effluent activity.

Owing to the short irradiation time, the sodium activity was too small to be detected, but the magnesium peak on elution with 1 N CH_3COOH was clearly shown. The whole separation took about 25 min.

In order to show the separation from sodium, a similar experiment was carried out in which a small amount of ^{22}Na was added to the feed solution, with the results shown in Fig. 1, in which two distinct peaks appear.

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[8] F. Gadda and G. Redaelli, *Energia Nucleare (Milan)* **7**, 701 (1960).

The independent yield of ^{96}Nb in the thermal neutron fission of ^{233}U, ^{235}U and ^{239}Pu

(*Received* 5 *August* 1960)

Niobium-96 is shielded by the stable ^{96}Zr and hence any observed in fission must arise by independent formation. The yield was first measured in the thermal neutron fission of ^{235}U by Cook[1]. The fractional chain yield of $9{\cdot}8 \times 10^{-5}$ was found to fall well below the value predicted by the Equal Charge Displacement rule.[2,3,4] Fig. 1 shows the charge distribution curve plotted with all the available independent yields for ^{233}U, ^{235}U and ^{239}Pu. These yields are given in the compilation by Croall[5]. The $Z-Z_P$ values were calculated using Glendenin's[2,3,4] simple formula and the Z_A curve given by Grummitt and Milton[6]. The values of $\bar{\nu}$ used were 2·5, 2·5 and 3·0[7] respectively for ^{233}U, ^{235}U and ^{239}Pu thermal neutron fission. The curve shown is the Gaussian

$$\eta = \frac{1}{\sqrt{1{\cdot}05\pi}} \cdot e^{-\frac{(Z-Z_P)^2}{1{\cdot}05}}$$

where η is the fractional chain yield.

This curve is a better overall fit to the points shown than that given by Glendenin[4]. The ^{96}Nb point is Cook's determination. It is clearly below the curve, and is in fact, as far as ^{235}U fission is concerned, the most outstanding deviation.

Pappas[3] and Wahl[9] have both made modifications to the charge distribution rule in an endeavour to fit the ^{96}Nb result to the curve. Pappas introduced discontinuities in the curve of Z_P plotted against mass in the region of shell closures which helped to explain the ^{96}Nb problem. Wahl, however, was able to show that from the values of the independent yields of other nuclides in the vicinity of the shell closures that there was no good evidence for the discontinuities in Z_P that Pappas postulated. Wahl then proposed that in ^{235}U fission a 50–42 proton split might be favoured at the expense of the neighbouring 51–41 and 49–43 proton splits. This would have the effect in uranium fission of reducing the independent yields of isotopes of niobium and technetium which have 41 and 43 protons respectively. However, in plutonium fission the favoured split would be 50–44 and the independent yields of niobium isotopes would be expected to be normal.

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An alternative explanation of the low independent yield of 23 hr ^{96}Nb may be found in the existence of another isomer of ^{96}Nb. Recent work has shown that for pairs of isomers one isomer is favoured in independent formation. For example, in the independent formation of ^{131}Te the high-spin (30 hr) isomer is formed at the expense of the low-spin isomer in the thermal neutron fission of ^{233}U, ^{235}U and ^{239}Pu[10]. In the case of ^{111}Pd, the low-spin isomer is favoured in the fission of ^{233}U and ^{239}Pu[11]. The low spin isomer of ^{106}Rh is also formed independently in preference to the high-spin isomer in the thermal neutron fission of ^{233}U and ^{239}Pu[12]. Another isomer of ^{96}Nb would be expected to be the lower spin state, and ORTH and SMITH[13] in the course of work on the short-lived isomers of niobium suggest that its half-life, if it exists, is less than 5 sec.

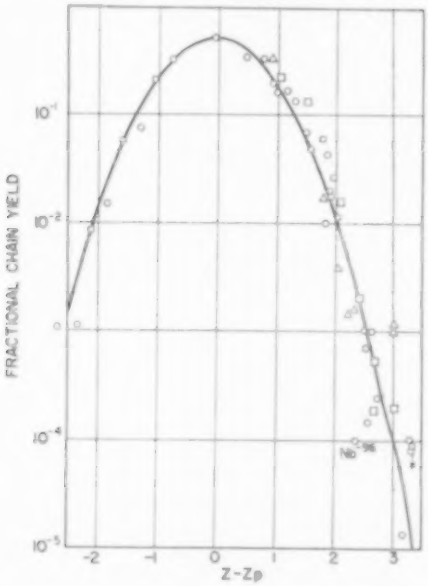

FIG. 1.—Charge distribution curve for thermal neutron fission
○ ^{235}U
△ ^{233}U
□ ^{239}Pu

In order to test WAHL's hypothesis it was decided to measure the independent yields of 23 hr ^{96}Nb in the thermal neutron fission of ^{233}U, ^{235}U and ^{239}Pu.

Experimental

The fissile materials were irradiated in solution in the BEPO pneumatic "rabbit". Irradiations were of 1 min duration so that the 50 min ^{95}Nb isomer could be detected, and a rapid zirconium-niobium separation would minimise the amount of short-lived niobium activities formed by decay of zirconium isotopes. The enriched (93%) ^{235}U was supplied by the Electromagnetic Separator Group at Harwell.

Niobium and zirconium carriers were added to the irradiated solution which was made up to a known volume. An aliquot (2–5%) of this solution was taken, added to barium carrier and set aside until the following day for barium analysis. A radio-chemical separation of the niobium was then carried out.

[10] M. TALAT-ERBEN, L. E. GLENDENIN and E. P. STEINBERG. Private communication (1958).
[11] L. E. GLENDENIN. Private communication (1959).
[12] I. F. CROALL and L. E. GLENDENIN. In press (1960).
[13] C. J. ORTH and R. K. SMITH, *J. Inorg. Nucl. Chem.* In press.

GLENDENIN[14] gave a separation scheme for niobium based on the precipitation of Nb_2O_5 from the soluble niobium oxalate complex by destruction of the oxalate with sodium chlorate in nitric acid solution. The scheme also included barium fluozirconate scavenging steps. This procedure gave only a relatively low decontamination from other fission products, notably tellurium and molybdenum. The procedure finally developed for this work was based on GLENDENIN's, but incorporated sulphide scavenging stages to remove molybdenum and tellurium more efficiently.

The barium separation scheme used was that given by GLENDENIN[15].

The final samples were mounted on a filter paper disc held in an aluminium tray. They were counted under an end window Geiger (window thickness 1·7 mg cm^{-2}) under identical geometry conditions. Source weights were arranged to be between 15 and 20 mg spread over an area of 2 cm^2. Corrections for self-absorbtion and backscatter were estimated to be less than 10 per cent and have been incorporated into the errors quoted on the results.

The decay of each sample was followed for about 10 days. The resulting decay curve showed half-lives of 50 min, 72 min and 23 hr. The results on the 50 min ^{95}Nb will be reported later. In this investigation only the 23 hr ^{96}Nb results were required, and these could be read directly from the decay curves. No significant contribution due to ^{95}Nb (35 days) was observed.

The independent yields were measured relative to the cumulative yields of Ba^{140} whose values in ^{233}U, ^{235}U and ^{239}Pu thermal neutron fission were taken[16] to be 6·0, 6·44 and 5·6 per cent respectively.

Results

^{233}U *thermal neutron fission*

Independent yield of 23 hr ^{96}Nb: $5{\cdot}8 \times 10^{-3}$%; $5{\cdot}6 \times 10^{-3}$%.
Average yield: $(5{\cdot}7 \pm 1{\cdot}0)10^{-3}$%.

^{235}U *thermal neutron fission*

Independent yield of 23 hr ^{96}Nb: $5{\cdot}9 \times 10^{-4}$%; $5{\cdot}8 \times 10^{-4}$%.
Average yield: $(5{\cdot}85 \pm 1{\cdot}0)10^{-4}$%.

^{239}Pu *Thermal neutron fission*

Independent yield of 23 hr ^{96}Nb: $3{\cdot}45 \times 10^{-3}$%; $3{\cdot}66 \times 10^{-3}$%.
Average yield: $(3{\cdot}6 \pm 0{\cdot}6) \times 10^{-3}$%.

Discussion

The total chain yields for mass 96 are 5·6% for ^{233}U, 6·0% for ^{235}U and 5·8% for ^{239}Pu thermal neutron fission[16]. Shown below are the ^{96}Nb independent yields expressed as fractions of the total chain yield.

^{233}U	^{235}U	^{239}Pu
$(1{\cdot}0 \pm 0{\cdot}2)10^{-3}$	$(9{\cdot}8 \pm 2{\cdot}0)10^{-5}$	$(6{\cdot}2 \pm 1{\cdot}0)10^{-4}$

These results may be compared with those of COOK[1] and TROUTNER[17].

	^{233}U	^{235}U	^{239}Pu
COOK	—	$9{\cdot}8 \cdot 10^{-5}$	—
TROUTNER	$(1{\cdot}3 \pm 0{\cdot}3)10^{-3}$	$(9{\cdot}5 \pm 2{\cdot}0)10^{-5}$	$(7{\cdot}7 \pm 1{\cdot}0)10^{-4}$

Fig. 2 shows these fractional chain yields plotted on the charge distribution curve. It will be seen that the plutonium fission result falls considerably below the curve, just as do the two uranium results.

[14] L. E. GLENDENIN, *The Fission Products* NNES, Div. IV, Vol. 9, Paper 253. McGraw-Hill, New York (1951)
[15] L. E. GLENDENIN, *The Fission Products* NNES, Div. IV, Vol. 19, Paper 288. McGraw-Hill, New York (1951).
[16] S. KATCOFF, *Nucleonics* **16**(4) 78 (1958).
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This would seem to indicate that the favoured 50–42 proton split is at any rate not an important factor in causing the low yield of 23 hr ^{96}Nb. In the absence of any direct evidence that the charge distribution curve for ^{239}Pu is the same as that for ^{235}U, TROUTNER[17] suggested that it might in fact be narrower, thus bringing the ^{96}Nb yield to within $\pm 0{\cdot}1$ charge units of the curve. However, a number of independent yield values for ^{239}Pu have recently become available[15] and these are also shown in Fig. 2. There is no reason to suggest that the charge distribution curve for plutonium is narrower than that for ^{235}U.

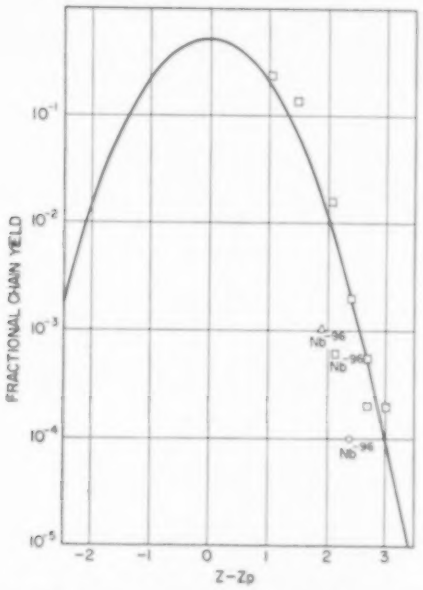

FIG. 2.—Curve from Fig. 1 showing ^{96}Nb fractional chain yields.
○ ^{235}U
△ ^{238}U
□ ^{239}Pu

The existence of a short lived isomer of ^{96}Nb,^{a} favoured in independent formation affords an alternative explanation of the low yield. Since its half-life would appear to be of the order of a few seconds[13] it will be very difficult to determine its independent yield. However, further work is planned to search for this isomer.

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High specific activity $^{35}SO_2$ from neutron irradiated CCl_4

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IN the course of an examination of the chemical consequences of the nuclear reaction $^{35}Cl(n,p)^{35}S$, it has been found that $^{35}SO_2$ of high specific activity could be recovered by appropriate scavenger techniques from thermal neutron irradiated carbon tetrachloride.

Since the presence of impurities in the target material is known[1] to have a pronounced effect on the chemical fate of the sulphur atom produced, the CCl_4 was rigorously purified by refluxing reagent grade material with mercury, followed by a triple distillation through an all-glass system. A centre cut was washed with 6 N NaOH and then exhaustively with distilled water. The washed material was dried with $CaCl_2$ and again distilled from $CaCl_2$ in an all-glass system. A centre cut was quickly transferred to a cold finger and carefully outgassed on a high vacuum line by the customary procedure. Of this stock supply, 0·25 mmole were transferred by high vacuum distillation into 0·88 cm^2 (0·5 cm i.d., 4·5 cm long) quartz ampoules which were provided with a break-off tip, and which had been thoroughly flamed and outgassed prior to filling.

These ampoules, together with a cobalt wire monitor (sealed in a quartz capillary) taped to the ampoule, were irradiated in the thermal neutron flux of the Industrial Reactor Laboratories reactor. The total nvt, calculated on the basis of a cross-section of 36·3 barns[2] for the reaction $^{59}Co(n,\gamma)^{60}Co$ was approximately $2{\cdot}9 \times 10^{17}$ n cm^{-2}. After a three-day cooling period which allowed the short-lived co-produced activities (mainly 37 min ^{38}Cl and 5 min ^{37}S, as well as 2·6 hr ^{31}Si from the quartz ampoule) to decay out, the ampoule was removed from the irradiation can, and after washing, placed into a cold finger arrangement which was attached to the high vacuum manifold. After evacuation, the capsule was opened with a magnetically operated weight and the volatile materials distilled into a liquid nitrogen cooled trap.

Two and a half millimoles of purified SO_2 were dosed into the trap which was then closed off from the remainder of the vacuum system. The trap was warmed to −78°C with an acetone–Dry-Ice bath and held at this temperature for 10 min to allow ample time for the system to come to equilibrium. At the end of this interval, the SO_2 was distilled from the −78°C trap into a second trap held at liquid nitrogen temperature. Thirty seconds was found to be an ample interval to effect essentially quantitative transfer.

The fact that the sulphur activity was present as $^{35}SO_2$ was demonstrated by a number of sensitive tests. These included not only low temperature distillation and radio assay of successive aliquots, but also preferential volatilization of SO_2 [compared to S(VI)] from an acidified aqueous solution of the scavenged sample.

The $^{35}SO_2$ so obtained was radio-assayed by standard procedures involving distillation of an aliquot into aqueous NaOH, followed by oxidation with Br_2 and precipitation of $Ba^{35}SO_4$. Thin samples (5–25 mg cm^{-2}) were counted under a Sugarman type gas flow counter fitted with a 0·5 mil, doubly aluminized mylar window. Corrections for self absorption, decay and geometry were applied and a final specific activity of 5×10^3 counts/min mg of $BaSO_4$ was observed in a replicate fashion. This corresponds to a source strength of 7·6 μc per mmole of SO_2. The radio chemical purity of the ^{35}S was determined by standard aluminium absorber techniques (since 14 day ^{32}P is co-produced in the target by the $^{35}Cl(n, \alpha)$ reaction). Impurity activities other than ^{35}S were found to comprise less than 1 part in 10^4 of the total.

The total amount of ^{35}S activity present in the target was calculated from the known cross-sections for the $^{35}Cl(n, p)$ and $^{59}Co(n, \gamma)$ reaction and the radioassay data for an aliquot of the monitor. Corrections for counting efficiency (0·065 for ^{35}S, 0·126 for ^{60}Co) were applied to these data, as well as a correction for chemical yield. These calculations showed that well over 90 per cent of the ^{35}S activity could be extracted by SO_2 scavenging.

The recovery of the bulk of the sulphur activity in the +4 oxidation state in these targets is consistent with the earlier findings by Koski *et al.*[1,2] that when thoroughly outgassed and moisture free KCl was irradiated with thermal neutrons, more than 80 per cent of the sulphur activity was carried in the non-sulphate form. Due to the absence of moisture and occluded gases in the irradiated CCl_4, it is unlikely that the final chemical fate of the sulphur archekine[4] in this system is SO_2. It is more likely that the recoiling ^{35}S atom comes to rest as S_2Cl_2 or perhaps SCl_2 and/or SCl_4. The formation of these thiohalogens is presumed to arise from the reaction of the archekine at or near the end of its recoil path with chlorine free-radicals in the target. These radicals in turn are expected to be present at relatively large steady state concentrations both as the result of the large γ-flux to which the target is exposed during the irradiation, as well as the elastic collisions and disruptive effects of the recoiling

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[3] T. A. Carlson and W. S. Koski, *J. Chem. Phys.* **23**, 1596 (1955).
[4] P. E. Yankwich, *Canad. J. Chem.* **34**, 301 (1956).

archekine itself. Hydrolysis of these sulphur chlorides by minute traces of moisture encountered in the post-irradiation treatment of the target material by the method discussed above is known[5] to lead to SO_2 as a major product as well as smaller amounts of S(O) and S(VI). The latter observation is consistent with our finding that the $^{35}SO_2$ isolated from the scavenged irradiated sample is contaminated to the extent of about 0·5 per cent with sulphur activity carried by sulphate scavenger.

In addition, the possibility that $^{35}SO_2$ is formed directly from the final chemical product by isotopic exchange with the added SO_2 cannot be excluded as a contributing mechanism. Although it is known[6] that isotopic sulphur exchange does occur between elementary sulphur and S_2Cl_2 in CCl_4 solution, no exchange studies in the systems SO_2-S_2Cl_2 and SO_2-SCl_2 appear to have been carried out. Indeed, on the basis of the extensive work of NORRIS and his co-workers[7] no ready exchange mechanism between the sulphur halides and SO_2 suggests itself, although such an exchange is thereby not conclusively ruled out.

The more quantitative aspects of the hot-atom processes in the present system are the subject of a continuing study. The author is grateful to Dr. DANIEL GREENBERG and The National Distillers Corporation for providing the neutron irradiations at the I.R.L. reactor and the U.S. Atomic Energy Commission for its continuing support.

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Fluorine nuclear spin resonance spectroscopy—IV
A silicon-29 isotope effect

(*Received* 9 *September* 1960)

WHEN fluorine is attached to a carbon atom bearing a heavy isotope such as D[1] or ^{13}C[2] or when it is joined directly to ^{13}C,[3] an "isotope effect" is observed which consists of a shift of the fluorine nuclear spin resonance (NSR) peak center in the direction of greater shielding, relative to the corresponding peak due to the "normal", (light) compound. Smaller effects in the same direction have been observed in proton NSR spectroscopy.[4,5,6]

Recently, a start has been made toward the theoretical explanation of such isotope shifts.[6] It is therefore of particular interest to examine more diverse examples of these effects, to provide experimental evidence concerning the relative importance of various parameters. In the present work the pair of isotopes compared, ^{28}Si and ^{29}Si, represent by far the most convenient choice from the second row of the periodic table. The hexa-co-ordinate fluosilicate anion was studied in aqueous solution.

Experimental

Ammonium fluosilicate (Harshaw Chem. Co.), 0·200 g, was dissolved in 0·80 ml of H_2O. The solution was rather acidic, pH 3·0 ± 0·3; in the preparation of the second sample a small amount of solid ammonium carbonate was added to adjust the pH to about 5·5, in order to inhibit the fluoride

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[5] G. V. D. TIERS, *J. Phys. Chem.* **64**, 373 (1960).
[6] H. S. GUTOWSKY, *J. Chem. Phys.* **31**, 1683 (1959).

exchange.[7] The solutions were filtered to remove any insoluble matter, and were placed in standard 5 mm o.d. NSR sample tubes.

A detailed description has been given of the NSR spectrometer and of the measurement techniques,[5] the latter having been developed for the detection of the similarly small ^{13}C—H isotope effect. All NSR work was done at 25·0°C. The doublet due to $^{29}SiF_6^{-2}$ was found to be centred at slightly higher field (more shielded) than the single very strong peak due to $^{28}SiF_6^{-2}$. Line widths W (in c/s) measured at half-maximal intensity, were quite reproducible but were pH-dependent, the, $^{29}SiF_6^{-2}$ peaks being relatively more broadened at low pH than the "image" peaks[5] derived from $^{28}SiF_6^{-2}$. The experimental results are presented in Table 1; all errors are expressed as the standard deviation of the averaged value.

TABLE 1.—THE EXCESS FLUORINE NSR SHIELDING, Δ, PRODUCED BY ^{29}Si IN AQUEOUS AMMONIUM FLUOSILICATE SOLUTIONS

pH	Δ, p.p.m.	J, c/s ($^{29}SiF_6^{-2}$)	No. of measurements	W, c/s $^{29}SiF_6^{-2}$ peaks	No. of measurements	W, c/s $^{28}SiF_6^{-2}$ image	No. of measurements
3.0	+0·004 ±0·003	108·37 ±0·25	12	1·37 ±0·03	22	0·97 ±0·02	44
5·5	+0·004$_3$ ±0·001$_2$	108·00 ±0·10	10	0·87 ±0·04	16	0·90 ±0·04	32

Discussion

It is seen from the results in Table 1 that the ^{29}Si—F isotope effect is so small as to be barely detectable. The ^{13}C—F effect is about thirty times as large,[2,3] indicative of a strong inverse dependence upon bond length. This point will be discussed more fully in a subsequent paper dealing with BH_4^- and BF_4^- isotope effects.[5]

MUETTERTIES and PHILLIPS[7] noted the acid-catalysed broadening (at very low pH) of the SiF_6^{-2} peak, which they attributed to "fluorine exchange between SiF_6^{-2} species", e.g. $HSiF_6^-$; exchange between SiF_6^{-2} anions would *not* cause any broadening. However, this hypothesis cannot account for the substantially greater broadening of $^{29}SiF_6^{-2}$ relative to $^{28}SiF_6^{-2}$ at low pH, shown in Table 1. From the stability constant for SiF_6^{-2} at pH 3·0[9] is it calculated that less than 0·1 per cent of the fluorine in the solution is present as fluoride ion, from which it follows that negligible broadening, and *no* differential broadening, would result from exchange with fluoride ion itself.

On the other hand, exchange of fluorine (perhaps *via* fluoride ion) between the isotopic fluosilicate anions would produce exactly the observed differential broadening of the $^{29}SiF_6^{-2}$ peaks. Since there is only a 2·3 per cent chance that a fluorine, once lost, will return to a $^{29}SiF_6^{-2}$ anion having similar spin the predominant process results in broadening; while for $^{28}SiF_6^{-2}$ the chance of such return is 95·4 per cent, hence broadening is slight. Stated otherwise, the rate constant, k ($\equiv 1/t_A$), calculated from the broadening of lines for "slow exchange"[10] must be corrected for the inherent probability of the process in question, if the true pseudo-first-order rate constant, k_1, is desired. Here $k_1 = k\,(^{29}SiF_6^{-2})/0{\cdot}977 = k\,(^{28}SiF_6^{-2})/0{\cdot}046$ from which one would expect the broadening of the $^{28}SiF_6^{-2}$ peak to be only 4·7 per cent as great as that for $^{29}SiF_6^{-2}$. While the data of Table 1 strongly confirm the expected differential broadening, the sample-to-sample reproducibility of line width measurements is insufficient for a critical test of the predicted ratio. The relatively precise differential broadening (Table 1) leads[10] to $k_1 = 3{\cdot}3 \pm 0{\cdot}1$ sec^{-1} (per fluorine atom) for loss of fluorine from fluosilicate ion at 25° and pH 3·0 ± 0·3. If, however, only the *first* fluorine is removed, giving species such as SiF_5OH^{-2}[7] or SiF_5^-, the rate constant listed above must be multiplied by six.

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Acknowledgement—I am greatly indebted to Mr. DONALD HOTCHKISS for the careful NSR spectral work exemplified by Table 1.

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Contribution No. 181 *from*
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A double sulphate of titanium and iron

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IN course of an investigation of the solution chemistry of titanium sulphates in aqueous and sulphuric acid solutions, a new double sulphate of titanium and ferrous iron has been isolated. Normal titanium sulphate, $Ti(SO_4)_2$, appears to be quite unstable,[1] but a number of double sulphate of titanium and bivalent metals such as Ca, Sr, Ba, Ni, Zn, Cu, and Mn, having the general formula $MSO_4.Ti(SO_4)_2$, have been reported.[2,3] MEHTA and PATEL[3] failed to prepare a double sulphate of titanium and iron.

Varying quantities of a solution of ferrous sulphate in 50% v/v sulphuric acid were added to a sulphuric acid solution of hydrated titanium oxide. On prolonged gentle heating (3–4 hr) shining deep-blue crystals began to separate slowly, the maximum yield being obtained when the weight ratio of TiO_2 and $FeSO_4.7H_2O$ in the sulphuric acid solution was of the order of 1 : 5. After cooling and decanting the supernatant liquid, the crystals were washed repeatedly with absolute alcohol to remove sulphuric acid. The crystalline product was then stored in a vacuum desiccator over sulphuric acid.

Determinations of titanium, iron and sulphate were carried out using a dilute hydrochloric acid solution of the product. The results of analysis of the product obtained on several occasions approximated to FeO—26·6, TiO_2—14·5, SO_3—58·3: required for $2FeSO_4.Ti(SO_4)_2$: FeO—26·4, TiO_2—14·7, SO_3—58·8.

The crystals are highly hygroscopic and easily decomposed by atmospheric moisture to a brownish mass. They are soluble in dilute mineral acids and acetic acid, and also in concentrated hydrochloric and nitric acids, but are insoluble in concentrated sulphuric acid. Ion-exchange methods showed the presence of Ti^{4+} and Fe^{2+} ions in dilute hydrochloric acid solution. On strong ignition a beautifully-coloured powdery mass was obtained which may be used as pigment.

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The chemical stability of tributyl phosphate in some nitrate and chloride systems

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TRIBUTYL phosphate (TBP) is a major solvent in the processing of nuclear fuels. It owes its success primarily to its chemical stability.[1] Generally, it is assumed[1] that the primary reaction between TBP and dilute aqueous acids (HNO_3 and HCl, for example) is a hydrolysis reaction; and it has been suggested that in the presence of concentrated acids the primary reaction may be a dealkylation reaction (i.e. $C_4H_9ONO_2$ and C_4H_9Cl are the products from TBP and HNO_3 or HCl, respectively).[1,2]

[1] L. L. BURGER, *The Chemistry of Tributyl Phosphate* HW-40910, (1955).
[2] W. H. BALDWIN *Chemical Division Annual Progress Report* p. 40. ORNL-2782- (1959).

BLUMENTHAL and HERBERT[3] in studying the hydrolysis of trimethyl phosphate limited the HCl concentration to ten mole percent of the ester concentration in order to suppress the dealkylation reaction. GERRARD *et al.* obtained excellent yields of alkyl halides using dry hydrogen halides on tertiary phosphates.[4]

Preliminary studies by the authors have disclosed two factors about the chemical stability of TBP which are very important to the processing of nuclear fuels. First, the so-called acid catalysed hydrolysis of TBP (equilibrated with 2–5 M acid) is not primarily a hydrolysis reaction, but a dealkylation reaction. Second, tributyl phosphate is degraded quite rapidly by (a) a homogeneous reaction with extracted zirconium (nitrate or chloride) and by (b) a heterogeneous reaction with solid zirconium compounds ($ZrO(NO_3)_2 \cdot 2H_2O$ or $ZrOCl_2 \cdot 8H_2O$). In both (a) and (b) either n-butyl nitrate or n-butyl chloride and insoluble zirconium organic phosphates are the major products.

A Pye Argon Chromatograph was used to detect and determine the amounts of the more volatile decomposition products. Samples were introduced into a four-foot column packed with acid washed, Johns–Manville Silocel firebrick which was coated with LAC-2R446 (25% by wt.).[5]

For each of the homogeneous reactions ,TBP was equilibrated with an equal volume of the aqueous solution at 50°C. In some experiments the aqueous phase was allowed to remain in contact with the organic phase; Table 1 indicates the aqueous and solid phases which were contacted with TBP and the principal products formed. At least three different zirconium organic phosphates were formed, one of which has been identified as $Zr(NO_3)_2(DBP)_2$.

TABLE 1.—TRIBUTYL PHOSPHATE DECOMPOSITION PRODUCTS

System	Principal products
2 to 5 M HNO_3—TBP	n-butyl nitrate, HDBP* and H_2MBP[1]
2 to 5 M HNO_3, 0·25 M Zr†—TBP	n-butyl nitrate, $Zr(NO_3)_2(DBP)_2$
Solid $ZrO(NO_3)_2 \cdot 2H_2O$—TBP	n-butyl, nitrate, zirconium organic phosphate
2·0 M HCl—TBP	n-butyl chloride, HDBP and H_2MBP[1]
2·0 M HCl, 0·25 M Zr†—TBP	n-butyl chloride, zirconium organic phosphate
Solid $ZrOCl_2 \cdot 8H_2O$—TBP	n-butyl chloride, zirconium organic phosphate

* HDBP is dibutyl monohydrogen phosphate; H_2MPB is monobutyl dihydrogen phosphate.
† $ZrO(NO_3)_2 \cdot 2H_2O$ and $ZrOCl_2 \cdot 8H_2O$ were used for preparation of zirconium solutions in nitrate and chloride systems, respectively.

The major conclusions which can be drawn at this time are:

(a) The primary TBP reaction over the acid ranges studied (2–5 M HNO_3; 2 M HCl) is not one involving hydrolysis.

(b) n-Butyl nitrate (the principal volatile product for nitrate systems) is an emulsifying agent and may be responsible for some of the emulsion problems encountered in fuel processing. Alkyl nitrates are also known to be unstable in the presence of acid and violent explosions may occur[6] when such systems are heated.[7]

(c) Zirconium extracted into the organic phase greatly accelerates TBP decomposition with the production of troublesome solid zirconium orgainc phosphates.

(d) Of the systems studied, TBP is degraded most rapidly by the heterogeneous reaction with solid zirconyl chloride or zirconyl nitrate.

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LETTERS TO THE EDITOR

Influence of the chelating agent on the separation of Eu^{3+} and Am^{3+} ions by solvent extraction*

(*Received* 29 *August* 1960)

AN EXTENSIVE investigation of the extraction of Eu(III) and Am(III) with various extracting agents and organic solvents, and with different compositions of the aqueous phase is being carried out at our laboratory. This paper reports some results which may be helpful for the separation of europium and americium in aqueous solutions.

Recently it has been shown by DYRSSEN and LIEM[1] that with dibutyl phosphate the net distribution ratio (chloroform/water) of Eu was larger than for Am, $q_{Eu} > q_{Am}$. The same result has now been obtained with TTA. However, with β-isopropyl tropolone we obtained $q_{Eu} \approx q_{Am}$ and with 5,7-dichloro-oxine $q_{Eu} < q_{Am}$. This gradual change of order seems to be parallel to the basicity of the ligand-forming atoms in the complexing agents: the oxygen atoms in di-n-butyl phosphate (pK_{HA} = 1·00) or its dimer, HA_2^-, and TTA ($pK_{HA} = 4{\cdot}43$ for the enol form) accept protons less readily than the oxygen atoms in β-isopropyl tropolonate ($pK_{HAB^+} \approx 0$, $pK_{HA} = 7{\cdot}04$), which in turn are less basic than the nitrogen and oxygen atoms in 5,7-dichloro-oxinate ($pK_{HAB^+} = 2{\cdot}89$, $pK_{HA} = 7{\cdot}47$).

The basic strength of the ligand can only be one of the factors that influence the separation of a lanthanide and an actinide ion with the same position in each series. It is known,[2] for example, that the hydrogen bond in tropolone is much stronger than in oxine and consequently this affects the relative basic strength of the two reagents. The hydrogen bond in acetylacetone[2] is still stronger. These and other effects in the chelation of actinide and lanthanide ions have been discussed by DYRSSEN[2,4,5]. Qualitatively, however, our results up till now suggest that an increase in basicity and chelating power (stability constant) of the ligand will increase q_{Am}/q_{Eu}. This relationship may facilitate the choice of a suitable chelating agent for the separation of ter-valent lanthanide and actinide ions by solvent extraction or paper chromatography.

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Vibrational spectrum of the $NCSe^-$ ion

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RECENT work on the infra-red spectra of HNCSe and DNCSe[1] led to an investigation of the vibrational frequencies of the selenocyanate ion. Several studies have been published on the infra-red

[1] To be reported at a later date.

and Raman spectra of the cyanate[2,3] and thiocyanate ions,[4,5] however, only two Raman frequencies have been reported for $NCSe^-$.[6,7]

KNCSe was prepared in the manner described by WAITKINS and SHUTT[8]. Samples were prepared both in Nujol mulls and in KBr pressed disks, and studied at 300° and 77°K. Infra-red spectra were recorded on a Perkin–Elmer Model 21 Spectrophotometer, using LiF, NaCl and CsBr prisms. Raman spectra were obtained with a Cary Model 81 Recording Spectrophotometer, using near-saturated solutions in 5 ml Raman tubes.

TABLE 1.—OBSERVED FREQUENCIES OF KNCSe
(Band centres given in cm^{-1})

	Infra-red (solid)		Raman (aqueous soln.)
	300°K	77°K	300°K
ν_1	558	559	558
ν_2 (*a*)	424	426	
ν_2 (*s*)	416	417	
ν_3	2070	2072	2075
ν_3 (C^{13})	2026	2027	
$\nu_3 + \nu_1$	2632		
$\nu_3 + \nu_2$ (*a*)	2491		
$\nu_3 + \nu_2$ (*s*)	2484		
$2\nu_2$ (*a*)	847	849	
$2\nu_2$ (*s*)	832	834	

Table 1 contains the observed frequencies. Fundamentals are numbered in the conventional manner.[9] The splitting of the bending frequency, ν_2, is assumed to arise from the crystal structure, as has been reported for KNCO[2] and KNCS.[4] Force constants were calculated, assuming a valence force field and distances of 1·22 Å and 1·83 Å for the N—C and C—Se bonds. Values obtained were $K_{CSe} = 3{\cdot}88$, $K_{CN} = 15{\cdot}1$, and $K\delta/r_1r_2 = 0{\cdot}25$, each $\times 10^5$ dynes/cm. The assignment of a weak band at 2026 cm^{-1} to the ν_3 fundamental of the ion containing C^{13} is supported by a calculated value of 2021 cm^{-1}.

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Regularities involving $^{6}_{2}$He and $^{4}_{2}$He and their possible implications for nuclear structure

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THE alpha-particle model of the nucleus, in which low-A nuclei are considered to consist of aggregates of α-particles, has been given fresh impetus by the recent work of WILDERMUTH and KANELLOPOULOS[1]

[1] K. WILDERMUTH and TH. KANELLOPOULOS, *Nucl. Phys.* **7**, 150 (1958).

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on their suggested cluster model of the nucleus. These authors pointed out that (i) clusters other $^4_2$He might be present in nuclei and (ii) stable closed shells such as those of $N = 50$ and $N = 82$ could be regarded as large clusters. The idea of clusters in the nuclear surface has also been discussed by WILKINSON[2] and MCCARTHY and PROWSE[3].

The possibility of $^6_2$He as a cluster was mentioned by AHRENS[4] and AHRENS and CHERRY[5] and it is the purpose of the present note to further discuss this possibility as well as that of $^4_2$He as a nuclear cluster. For this purpose, regularities involving a variety of types of evidence have been sought and examined. The type of evidence is listed below together with the source of the relevant regularity:

(i) systematics of stable isotopes (AHRENS and CHERRY[5], AHRENS[6])
(ii) relative abundances of isotopes (AHRENS[4])
(iii) energies of excited states (CHERRY[7])
(iv) neutron and proton separation energies (CHERRY[7])
(v) mass excess and binding energy (AHRENS[6,8])
(vi) half lives of longlived α-active nuclei (PERLMAN *et al.*[9], STUDIER and HUIZENGA[10] and AHRENS[6]).

The great majority of the regularities begin or end with a well established magic number and are associated with increases of $^6_2$He $(2p + 4n)$ sub-units as well as the more familiar $^4_2$He; the $^6_2$He regularities involve a maximum of seven participants. A condideration of the regularities leads to the suggestion that if clusters occur in the nuclear surface—or perhaps within the structure—both $^6_2$He and $^4_2$He should be considered as possible clusters; and, if so, the regularities indicate a threefold division of nuclei with respect to Z and N as follows:

(i) *A $^4_2$He (or α-particle) region*
Up to $Z = N = 20$, with $^4_2$He as the principal cluster. Shell closure (possibly of clusters) takes place at $Z = N = 20$.

(ii) *A transition region*
$Z = N = 20$ to $N = 50$. $^4_2$He and $^6_2$He as clusters outside a closed shell. The transition region is itself sub-divided (AHRENS[6]).

(iii) *A $^6_2$He region*
$N = 50$ to $N = 152$. $^6_2$He is regarded as the principal cluster after shell closure at $N = 50$. (The $^6_2$He regularities are most highly developed between $N = 50$ and $N = 82$.)

If it is assumed that heavy nuclei ($N > 50$) of a given type are "built" by adding $^6_2$He to the nuclear surface, the rate of increase of N–Z is a little too rapid for stability to be maintained over a large range of Z and an examination of the $^6_2$He regularities leads to the suggestion that one function of $N = 82$ and certain other significant neutron numbers may be to reduce neutron excess.

A full account of the above will be given elsewhere.

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The nuclide ^{182}Hf[1]

(*Received* 11 *October* 1960)

THE nuclide ^{182}Hf has been made by thermal-neutron irradiation of hafnium oxide and has been found to have a half-life of $8{\cdot}5 \times 10^6$ years. A preliminary study has been made of possible radiations associated with the nuclide.

[1] This work was performed under the auspices of the U.S. Atomic Energy Commission.

In early 1955, a 2 g sample of hafnium oxide was irradiated in a thermal-neutron flux of about 2×10^{14} cm^{-2} sec^{-1} for two months at the Materials Testing Reactor at Idaho Falls, Idaho. The radioactivity in the sample was allowed to decay for four years before the investigation was begun.

In 1959, the sample was dissolved in hydrofluoric acid and purified by extraction into thenoyltrifluoracetone ("TTA") from 2 N HCl, then separated from zirconium by selective elution of the latter from a Dowex-50 cation exhange resin with 1 N H_2SO_4.

Elucidation of the ^{182}Hf was then made by observation of the growth of the ^{182}Ta daughter, by γ-ray pulse-height analysis, and by mass-spectrometric analysis. These are described in order below.

A purified sample of HfO_2 weighing 106 mg was observed with a sodium iodide (Tl) scintillation counter equipped with variable-energy channel setting. This channel was set for the 1·1–1·2 MeV transitions of ^{182}Ta. Over a period of 250 days, growth was observed which corresponded to a daughter with a 110 day half-life. As a check on the behavior of the detector, a sample of ^{182}Ta (made by thermal-neutron irradiation of tantalum foil) was observed whenever the sample of HfO_2 was counted. Behaviour was normal, the decay corresponding to the known 110 day half-life for ^{182}Ta. Thus the existence of the parent ^{182}Hf was established from the daughter growth. By comparison of a ^{182}Ta source in this particular energy channel with a 4π beta count, the disintegration rate of the daughter—and therefore of the parent—was established. It was found that the saturation specific activity was 40 dis/min per mg of sample.

γ-Ray pulse-height analysis showed that about half of the activity was due to residual ^{175}Hf, the remainder to a number of γ-rays, none above 0·56 MeV. One prominent photopeak at 0·27 MeV might be the same as that noted by GROSHEV *et al.*[2] in the neutron-capture gamma spectrum of tantalum, but the other photopeaks do not correspond to any of those listed. At the present time it is not known whether any of the observed photopeaks can actually be associated with ^{182}Hf. Work is continuing on the characterization of the γ-radiation in the sample.

A small specimen of the hafnium was analysed in the two-stage mass spectrometer at the Vallecitos Laboratory of the General Electric Company and found to contain 0·0088 atom per cent abundance at the mass 182 position. A small background correction was applied by a similar analysis of unirradiated hafnium. On the basis of the atomic abundance and the specific activity of the sample, a half-life of $8{\cdot}5 \times 10^6$ years was calculated for ^{182}Hf.

Dr. ROBERT NAUMANN of Princeton University has informed us that he has made an investigation somewhat similar to ours and also has concluded that ^{182}Hf is a nuclide of long half-life.

Acknowledgements—The authors are indebted to Mr. VINCENT SCOTTI and his co-workers of the Pratt and Whitney Aircraft Corporation for use of their hot cells in the early stages of the handling, and to Dr. WARD ALTER, Mr. E. L. KRAMER and their co-workers for the precise determination of the isotopic composition of the irradiated hafnium, without which the half-life could not have been determined.

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ERRATA

1. B. P. BLOCK, The reaction of hexamminecobalt(III) chloride with sodium cyanide, *J. Inorg. Nucl. Chem.* **14,** 294–295 (1960).

   The second sentence of the second paragraph on p. 295 should read as follows: "The addition of 6·1 g of $K_3[Co(CN)_6]$ (prepared as described in Inorganic Synthesis[10]) dissolved in 150 ml of H_2O to a solution of 5·0 g of $[Co(NH_3)_6]Cl_3$ in 100 ml of H_2O at room temperature gave a precipitate of 6·4 g of $[Co(NH_3)_6][Co(CN)_6]$."

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   p. 216, 3rd paragraph, 7th line: for "contamination of 0·001 μc of ^{90}Sr in 100 μc of ^{90}Y" read "contamination of 0·001 μc of ^{90}Sr in 100 mc of ^{90}Y".

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(a) *J. Inorg. Nucl. Chem.* **9**, 252 (1959); **11**, 124 (1960);

(b) *Talanta* **3**, 219 (1960)

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I should like to record my gratitude to him for his guidance and criticism in this work, which is of course in his long-standing area of interest, and to express regrets for the previous omission of his name from these papers.

Alplaus, N. Y. PETER CANNON

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